DIE KOLLOIDCHEMISCHEN UNTERSUCHUNGEN DER SYSTEME VON DREI FLÜSSIGEN KOMPONENTEN.

I. ÜBER DAS KOLLOIDVERHALTEN KRITISCHER GEMISCHE VON DREI FLÜSSIGKEITEN.

Von Naoyasu SATA und Osamu KIMURA.

Eingegangen am 28. Mai, 1935. Ausgegeben am 28. September, 1935.

Einleitung.

Wenn eine Substanz von der molekularen Dimension zur makroskopischen Dimension übergeht, ist es ganz klar, dass sie inzwischen von der Kontinuitätsvorstellung aus die "Kolloid-Dimension" durchlaufen wird. Das dürfte auch das Grundprinzip der bekannten von Weimarn'schen Theorie "Allgemeinheit des Kolloidzustandes"[1] sein.

Der einfachste Fall trat schon ein beim kritischen Punkt der Phasengrenze einer reinen Substanz, wie schon von vielen Autoren[2] bemerkt wurde. Neulich hat Wo. Ostwald[3] ein recht schönes, zusammenfassendes Übersichtsbild über dieses Thema vom Standpunkt der Kolloidchemie ausgegeben. Aber solches kolloides System ist jedenfalls ein metastabiles System, das man nicht lange stabil halten kann. Ganz ähnlich kann man auch die kritischen Gemische zweier Flüssigkeiten betrachten. Wo. Ostwald[4] hat auch solche Fälle untersucht um seine Theorie von der Strukturviscosität zu beweisen. Weiter wissen wir von solchen Fällen wie die kritischen Flüssigkeitsgemische, wo das System drei flüssige Komposente enthält, von denen zwei Flüssigkeiten gegeneinander nicht oder begrenzt mischbar sind und wo die dritte mit jeder anderen unbegrenzt mischbar ist. Wenn man hier annimmt, dass einer von den Komponenten keine Flüssigkeit sondern eine feste Substanz wäre, dann entspricht dieser Fall der Herstellungsmethode kolloider Lösungen durch Wechseln des Lösungsmittels, die von P. P. von Weimarn und N. von Weimarn[5] entwickelt worden ist. Bei der Phasenregel-Unter-

CHEMISTRY HALL LIBRARY

(1) P. P. von Weimarn, „Die Allgemeinheit des Kolloidzustandes", Dresden und Leipzig, 1925; *Kolloid-Z.*, **53** (1930), 246.

(2) W. H. Keesom, *Ann. Phys.*, (4), **35** (1911), 591. Wo. Ostwald, *Ann. Phys.*, (4), **36** (1911), 848. I. Traube, *Ann. Phys.*, (4), **8** (1902), 267; *Kolloid-Z.*, **70** (1935), 302. P. Hein, *Z. physik. Chem.*, **86** (1914), 385.

(3) Wo. Ostwald, *Kolloid-Z.*, **64** (1933), 50.

(4) Wo. Ostwald und Malss, *Kolloid-Z.*, **63** (1933), 61.

(5) N. von Weimarn, *Kolloid-Z.*, **54** (1931), 296.

suchung vom System Benzol-Wasser-Alkohol hat Bancroft[6] schon darauf hingewiesen, dass das System beim kritischen Punkt ein typisch kolloides Aussehen, d. h. opaleszierende bläulichweisse Trübung zeigt. V. Rothmund[7] und J. Friedländer[8] haben auch einige solche Fälle studiert und die Viscositätsmessungen u.s.w. ausgeführt. Neulich hat M. Pestemer[9] die Viscosität vom System Benzol-Wasser-Alkohol gemessen. Diese Messung ist aber unter Rührung von 800 Umdrehungen per Minute ausgeführt, und auf das kolloide Verhalten des Systems ist nicht besonders geachtet worden.

Folgende Untersuchung wurde ausgeführt um solche Systeme von drei flüssigen Komponenten zu systematisieren vom Standpunkt der Kolloidchemie aus und um weitere kolloidchemische Eigenschaften solcher emulsoiden Suspension zu studieren.

Experimenteller Teil.

Das Verhalten der oben erwähnten Systeme von drei Komponenten, nämlich, dass die eine Flüssigkeit mit der zweiten begrenzt oder fast unmischbar ist und das die dritte mit anderen in allen Verhältnissen mischbar ist, können wir allgemein nach der Phasenregel schematisch wie Abb. 1 zeigt, ausdrücken. A und B bedeuten zwei nicht oder begrenzt mischbare Flüssigkeiten und C ist eine mit A und B in allen Verhältnissen mischbare Flüssigkeit. Die kritische kolloiddisperse Phase trat nahe der Grenzkurve ein, wenn man zu einem beliebigen Gemisch vorsichtig den dritten Komponenten einführte. Für den idealen Fall, wo das System ziemlich stabil im Kolloid-Gebiet bleiben würde, verläuft die Änderung folgendermassen.

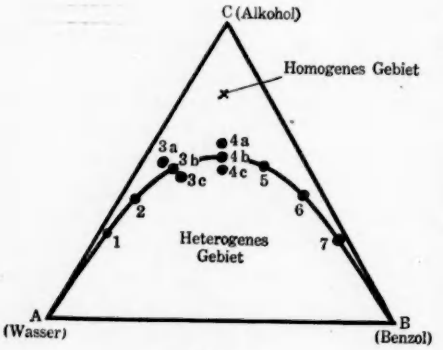


Abb. 1.

Das anfangs ganz klare homogene System wird erst schwach bläulich, danach opaleszierend bläulich und dann bläulichweiss trübe.

(6) Bancroft, *Phys. Rev.*, **3** (1895), 21.
(7) V. Rothmund, *Z. physik. Chem.*, **63** (1908), 54.
(8) J. Friedländer, *Z. physik. Chem.*, **38** (1901), 435.
(9) M. Pestemer, *Kolloid-Z.*, **65** (1933), 25.

Die Trübung wird mehr und mehr beim Zusatz dritter Komponente und endlich scheiden Flüssigkeitstropfen aus, und das System trennt sich in zwei ganz klare Flüssigkeitsschichten.

Wenn man umgekehrt beginnt mit einem zweiflüssigen heterogenen System, das sich anfangs leicht wieder in zwei klare Flüssigkeiten trennt, dann wird es zuerst eine schwer wieder trennbare Milch, dann verschwindet nach und nach diese weisse Trübung und dabei erhält dieses System einen bläulich opaleszierenden Ton, der endlich auch verschwindet, sodass eine ganz klare homogene Flüssigkeit bleibt.

Vorversuche. Wir haben zuerst das Vorhandensein solches kolloiddispersen Gebietes bei verschiedenen Systemen (gekennzeichnet durch bläuliche Opaleszenz bzw. Tyndall-Kegel) in Thermostaten von 30°C. untersucht. Als eine von den unmischbaren Flüssigkeiten haben wir Wasser benutzt, dann wird der zweite Komponent zu Benzol, seine Derivate und andere unpolare Flüssigkeiten fixiert. Als dritter Komponent soll demgemäss Alkohol bzw. Aceton ausgewählt werden.

Die zusammenfassenden Resultate unserer Versuche sind in Tabelle 1 ersichtlich.

Tabelle 1.

Komponent C / Komponent B	Methylalkohol	Äthylalkohol	*n*-Propylalkohol	*i*-Propylalkohol	Aceton
Benzol	+++	+++	+	+	−
Toluol	++	++	++	+	−
Äthylbenzol	++	++	+	+	−
Chlorbenzol	+	+	?	+	−
Nitrobenzol	+	+	?	+	−
Anilin	+	+	?	+	−
o-Xylol	+	+	+	+	−
m-Xylol	+	+	+	+	−
p-Xylol	+	+	+	+	−
Cyclohexan	+	+	?	+	−
n-Pentan	−	−	−	−	−
n-Hexan	−	−	−	−	−
Tetrachlorkohlenstoff	++	++	+	+	−
Chloroform	++	++	+	+	−
Schwefelkohlenstoff	++	++	+	+	−
Chloräthylen	+	+	?	+	−
Äthyläther	−	−	−	−	−

Durchschnittlich haben wir solche Systeme in drei Gruppen klassifiziert, nämlich

(a) bläulich opaleszierendes kolloides Gebiet, das ziemlich lang stabil ist in bezug auf Änderung (Zusatz) eines dritten Komponenten, in der Tabelle mit ++ bzw. +++ bezeichnet;

(b) bläulich opaleszierendes Gebiet, das aber sehr unstabil ist und bei dem die Opaleszenz gleich wieder verschwindet gegen winzigste Änderung dritter Komponente (0.02 c.c.) In der Tabelle mit + ausgedrückt;

(c) bläulich opaleszierendes Gebiet konnten wir in der Genauigkeitsgrenze unserer Versuche (0.02 c.c.) nicht erhalten. In der Tabelle mit − bezeichnet.

Aus der Tabelle merkt man gleich, dass als Komponent B das Benzol und seine Alkyl-Derivate, wie z. B. Toluol und Äthylbenzol und auch unpolare Flüssigkeiten, wie z. B. Tetrachlorkohlenstoff, Schwefelkohlenstoff und Chloroform gegen Methyl- bzw. Äthylalkohol als Komponent C, das beste Resultat zeigt. Chlor-, Nitro- oder Amino-Derivate des Benzols geben nicht mehr so ausgezeichnete Resultate. Merkwürdigerweise geben Pentan und Hexan negative Resultate, obwohl sie unpolar sind, wohingegen die anderen unpolaren Flüssigkeiten, wie Benzol, Tetrachlorkohlenstoff, Chloroform u.s.w. positive Resultate geben. Hier könnte man vermuten, dass diese Erscheinung mit der chemischen Struktur zusammenhängt, wenn man beachtet, dass Pentan und Hexan Ketten-Struktur besitzen und die anderen oben genannten unpolaren Flüssigkeiten ringförmige oder symmetrische Struktur aufweisen. Hier zeigt das Aceton wieder eine Anomalie, wie von einem von uns an anderer Stelle[10] oft bemerkt worden ist. Bei Äther bleiben uns auch als Ausnahme die negativen Resultate, deren Ursache wir auch einmal studieren möchten.

System: Benzol-Wasser-Äthylalkohol. Durch oben ausgeführte qualitative Versuche ist es uns jetzt bekannt, dass die Systeme Benzol-Wasser und Äthyl- bzw. Methylalkohol grössten Bereich stabiler kolloider Systeme besitzt. Die quantitative Untersuchung des Systems wurde zunächst ausgeführt.

Der gebrauchte Alkohol wurde folgendermassen gereinigt: Verkäuflicher reinster 95%iger Alkohol wird erst mit Kaliumpermanganat behandelt und mit CaO für einen Tag mit Rückflusskühler gekocht und dann destilliert. Der erhaltene Alkohol hat das spezifische Gewicht

(10) N. Sata und K. Kurano, *Kolloid-Z.*, **65** (1933), 283. N. Sata und S. Watanabe, *Kolloid-Z.*, **70** (1935), 159.

0.7865 bei 25°C., also 99.53% Reinheit. Das Benzol, und zwar das Merck'sche Präparat "rein kristallisierbar" wurde über Na-Metall destilliert. Das Wasser ist ein zweimal destilliertes Leitfähigkeitswasser nach Bourdillon.[11]

Das Dreieckdiagramm des Systems Benzol-Wasser-Äthylalkohol ist schon sehr oft vom Standpunkt des Phasenregels[12] aus studiert, wie auf Abb. 1 schematisch wiedergegeben ist.

Um das Verhalten bei kritischen Punkten zu studieren, haben wir folgende Versuche angestellt. Denken wir an die verschiedenen Punkte 1–7 auf der kritischen Grenzkurve. Um jeden dieser Punkte haben wir noch einige Punkte 1a, 1b, 1c u.s.w. durch kleine Veränderung (0.02 c.c.) eines Komponenten hergestellt, die in die Probiergläschen 15 mm. Durchmesser und 200 mm. Länge eingeschmolzen sind. Diese Proben wurden dann in Thermostat von 30°C. getaucht und beobachtet. Nach einiger Zeit teilten sich einige Proben in zweiflüssige Systeme. Aber bei einigen bleibt das bläulich bis schwach weissgetrübte bläulich opa-

Tabelle 2.

	C_2H_5OH (c.c.)	%	C_6H_6 (c.c.)	%	H_2O (c.c.)	%	Zustand
1 a	2.00	—	10.00	—	0.12	—	homogen
1 b	2.00	—	10.00	—	0.16	—	homogen
1 b′	2.00	16.58	10.00	82.11	0.18	1.31	weisslich trübe
1 c	2.00	—	10.00	—	0.20	—	weisslich trübe
1 d	2.00	—	10.00	—	0.24	—	weisslich trübe
1 e	2.00	—	10.00	—	0.30	—	weisslich trübe

Tabelle 3.

2 a	5.00	—	10.00	—	0.66	—	homogen
2 a′	5.00	31.85	10.00	63.69	0.68	4.46	bläul. opaleszierend
2 b	5.00	—	10.00	—	0.70	—	bläul. opaleszierend
2 c	5.00	—	10.00	—	0.74	—	bläul. opaleszierend
2 d	5.00	—	10.00	—	0.78	—	bläul. opaleszierend
2 e	5.00	—	10.00	—	0.82	—	bläul. opaleszierend
2 e′	5.00	31.57	10.00	63.13	0.84	5.30	weisslich trübe
2 f	5.00	—	10.00	—	0.86	—	weisslich trübe
2 g	5.00	—	10.00	—	0.90	—	weisslich trübe

(11) R. Bourdillon, *J. Chem. Soc.*, **103** (1913), 791.
(12) Bancroft, *loc. cit.* Lincoln, *J. Phys. Chem.*, **4** (1900), 161. Barbandy, *Rec. trav. chim.*, **45** (1913), 207. Holmes, *J. Chem. Soc.*, **113** (1918), 263. Bogin, *J. Ind. Eng. Chem.*, **16** (1924), 380.

Tabelle 4.

	C_2H_5OH (c.c.)	%	C_6H_6 (c.c.)	%	H_2O (c.c.)	%	Zustand
3 a	5.00	—	5.00	—	1.06	—	homogen
3 a′	5.00	45.13	5.00	45.13	1.08	9.74	bläul. opaleszierend
3 b	5.00	—	5.00	—	1.10	—	bläul. opaleszierend
3 c	5.00	—	5.00	—	1.14	—	bläul. opaleszierend
3 d	5.00	—	5.00	—	1.18	—	bläul. opaleszierend
3 e	5.00	—	5.00	—	1.20	—	bläul. opaleszierend
3 e′	5.00	44.60	5.00	44.61	1.21	10.79	weisslich trübe
3 f	5.00	—	5.00	—	1.22	—	weisslich trübe
3 g	5.00	—	5.00	—	1.24	—	weisslich trübe

Tabelle 5.

4 a	10.00	—	5.00	—	3.44	—	homogen
4 b	10.00	—	5.00	—	3.48	—	homogen
4 c	10.00	—	5.00	—	3.52	—	homogen
4 c′	10.00	53.94	5.00	6.97	3.54	19.09	weisslich trübe
4 d	10.00	—	5.00	—	3.56	—	weisslich trübe
4 e	10.00	—	5.00	—	3.60	—	weisslich trube

Tabelle 6.

5 a	10.00	—	2.00	—	5.50	—	homogen
5 b	10.00	—	2.00	—	5.60	—	homogen
5 c	10.00	—	2.00	—	5.70	—	homogen
5 c′	10.00	56.34	2.00	11.26	5.75	32.40	weisslich trübe
5 d	10.00	—	2.00	—	5.80	—	weisslich trübe
5 e	10.00	—	2.00	—	5.90	—	weisslich trübe

Tabelle 7.

6 a	5.00	—	0.20	—	5.00	—	homogen
6 b	5.00	—	0.25	—	5.00	—	homogen
6 c	5.00	—	0.30	—	5.00	—	homogen
6 c′	5.00	48.54	0.33	2.91	5.00	48.55	weisslich trübe
6 d	5.00	—	0.35	—	5.00	—	weisslich trübe
6 e	5.00	—	0.40	—	5.00	—	weisslich trübe

Tabelle 8.

	C_2H_5OH (c.c.)	%	C_6H_6 (c.c.)	%	H_2O (c.c.)	—	Zustand
7 a	5.00	—	0.04	—	10.00	—	homogen
7 b	5.00	—	0.08	—	10.00	—	homogen
7 b′	5.00	33.11	0.10	0.66	10.00	66.23	weisslich trübe
7 c	5.00	—	0.12	—	10.00	—	weisslich trübe
7 d	5.00	—	0.16	—	10.00	—	weisslich trübe

leszierende, typische kolloide Aussehen unverändert stabil. Die Versuchsergebnisse sind in den Tabellen 2–8 zusammengestellt.

Wenn man die Punkte, wo bläulich opaleszierende Gemische angegeben sind, auf Dreieckdiagramme überträgt, erhält man eine schmale Insel nahe der Grenzkurve, wie in Abb. 2 ersichtlich ist. Alle beliebigen Punkte der in dieser Insel ausgedrückten Gemische bleiben bläulich opaleszierend kolloidal bei 30°C. Es ist zu beachten, dass sich das kolloidstabile Gebiet an der Alkohol-Benzol-Axe, d. h. an der wasserarmen Gegend des Dreieckdiagramms befindet, und dass in dem benzolarmen Gebiet über der kritischen Kurve keine stabile bläulich opaleszierende Emulsion zu erhalten ist.

Dann haben wir den Temperaturbereich der Stabilität dieser Emulsionen untersucht. Wir tauchen z. B. 3b, 3e, 2b, 2e ins Wasserbad und beobachten während der Änderung der Temperatur die Obergrenze, wo

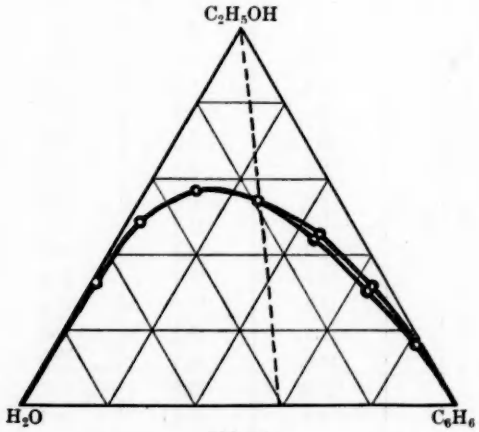


Abb. 2.

Tabelle 9.

	Obergrenze °C.	Untergrenze °C.
2 b	22	14
2 e	44	29
3 b	33	20
3 e	42	29

die bläuliche Opaleszenz gerade verschwindet und das System homogen wird, und die Untergrenze, wo das System weisslich trübe wird und sich in zwei Schichten scheidet. Die Ergebnisse sind gegeben in Tabelle 9. Man sieht aus Tabelle 9, dass ein System während des Temperaturbereichs

Tabelle 10.
Initiale Zusammensetzung
= 1.0 c.c. H_2O+10.0 c.c. C_6H_6

Zugefügte Alkohol (c.c.)	Volum der Unterschicht (c.c.)	Total-Volum (c.c.)
0	1.0	11.0
1.0	1.4	12.0
2.0	1.8	13.0
3.0	2.3	14.0
4.0	3.1	15.0
5.0	4.1	16.0
5.5	4.8	16.5
6.0	17.0	17.0

Tabelle 11.
Initiale Zusammensetzung
= 2.0 c.c. H_2O+10.0 c.c. C_6H_6

0	2.0	12.0
1.0	2.6	13.0
2.0	3.4	14.0
3.0	4.1	15.0
4.0	4.9	16.0
5.0	5.8	17.0
6.0	6.9	18.0
6.5	7.6	18.5
7.0	8.3	19.0
7.5	9.1	19.5
8.0	10.2	20.0
8.5	11.5	20.5
9.0	13.9	21.0
9.5	21.5	21.5

Tabelle 12.
Initiale Zusammensetzung
= 2.0 c.c. H_2O+5.0 c.c. C_6H_6

Zugefügte Alkohol (c.c.)	Volum der Unterschicht (c.c.)	Total-Volum (c.c.)
0	2.0	7.0
1.0	2.7	8.0
2.0	3.5	9.0
3.0	4.5	10.0
4.0	5.7	11.0
5.0	7.3	12.0
5.5	8.4	12.5
6.0	9.5	13.0
6.5	11.0	13.5
7.0	13.0	14.0
7.5	14.5	14.5

Tabelle 13.
Initiale Zusammensetzung
= 5.0 c.c. H_2O+5.0 c.c. C_6H_6

0	5.0	5.0
1.0	5.8	6.0
2.0	6.8	7.0
3.0	7.7	8.0
4.0	8 6	9.0
5.0	9.6	10.0
6.0	10.7	11.0
7.0	11.9	12.0
8.0	13.3	13.0
9.0	14.7	14.0
10.0	16.3	15.0
11.0	18.1	16.0
12.0	20.2	17.0
13.0	22.3	18.0
14.0	19.0	19.0

Tabelle 14.
Initiale Zusammensetzung
= 4.0 c.c. H_2O+2.0 c.c. C_6H_6

Zugefügte Alkohol (c.c.)	Volum der Unterschicht (c.c.)	Total-Volum (c.c.)
0	4.0	6.0
1.0	4.9	7.0
2.0	5.9	8.0
3.0	7.0	9.0
4.0	8.1	10.0
5.0	9.2	11.0
6.0	10.4	12.0
7.0	11.8	13.0
8.0	13.3	14.0
8.5	14.3	14.5

von etwa 10 Grad stabil opaleszierend bleibt, wenn es eine geeignete Zusammensetzung besitzt. Vergleicht man Abb. 2 und Tabelle 9, so kann man auch bemerken, dass der Temperatureinfluss sehr empfindlich ist, besonders hinsichtlich der Anderung von Wassergehalt, und zwar sind wasserarme Gemische bei niedrigerem Temperaturbereich stabiler als wasserreiche Gemische, trotzdem es nur ein sehr kleiner Unterschied an Wasser von 1.5 bis 2.0% ist.

Um das Verhalten zwischen Änderung der Komponente und Phasenzustand klarzumachen, haben wir weiter folgende Versuche angestellt: In die langen Probiergläser mit geschliffenen Stöpseln (30 cm. Länge und 1 cm. Durchmesser) nehmen wir verschiedene Kombinationen von Benzol und Wasser, die sich natürlich in zwei Schichten befinden, Benzol oben und Wasser unten. Fügt man den Alkohol tropfenweise dazu, erfolgt die Änderung des Volumens beider Schichten, bis sich endlich das System homogen mischt. Der Versuch wurde ausgeführt in einem Thermostat von 20°C. Die Ergebnisse sind in Tabellen 10–14 und Abb.

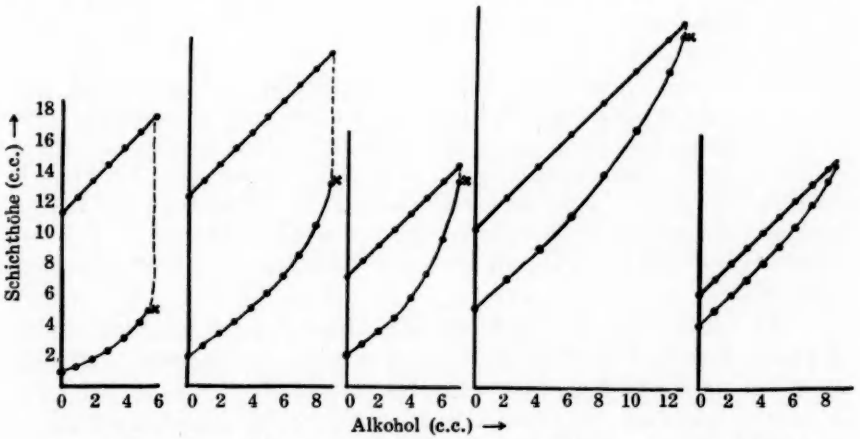


Abb. 3. Abb. 4. Abb. 5. Abb. 6. Abb. 7.

3–7 zusammengestellt. Bei der mit × bezeichneten Zusammensetzung findet ein Platzwechsel beider Schichten statt. (In der Abbildungen wurde es der Einfachheit halber so dargestellt, als ob kein Platzwechsel geschehen wäre). Nach dem Platzwechsel steigt das Volumen einer Schicht durch einen kleinen Alkoholzusatz sehr schnell an, und endlich wird das ganze System homogen und entwickelt sich in dieser Nähe zum bläulich opaleszierenden System. Bei dem wasserreichen System steigt die Kurve anfangs steiler an und an der Stelle des Platzwechsels ist die eine Schicht schon sehr klein im Vergleich zu der anderen Schicht (Abb. 5 und 6). Bei dem System, das mehr als 50% Wasser enthält, findet überhaupt kein Platzwechsel statt. Wenn man die auf Abb. 7 bezeichneten Punkte auf das Dreieckdiagramm von Abb. 2 überträgt, so sieht man sofort, dass sie ausserhalb der Emulsions-Insel fallen: Wenn man auf der Abb. 2 die Alkohol-Spitze mit der Insel-Spitze verbindet, dann trifft die Linie ungefähr auf 40% Wasser, und es ist klar, dass bei mehr als 40% Wasser es unmöglich ist, eine stabile Emulsion zu erhalten. Die entsprechenden Punkte von Abb. 7, die bei 60% Wasser angefangen war, fallen natürlich nicht in die Emulsions-Insel hinein.

Erörterung.

Von den oben ausgeführten Experimenten über das Verhalten dieses dreiflüssigen Systems in der Nähe kritischer Punkte möchten wir Folgendes schliessen:

(1) Die Verteilung von Alkohol zwischen Benzol und Wasser scheint nicht gleich zu sein, und zwar nimmt das Wasser viel stärker Alkohol auf als das Benzol.

(2) Denn, wenn man Abb. 3–7 vergleicht, so nimmt bei der Wasserschicht das Volumen viel mehr zu als bei der Benzolschicht beim Alkoholzusatz. Und der Platzwechsel beider Schichten bei den kritischen Punkten findet auch deshalb statt, weil das Wasser ($d = 1.000$) den Alkohol ($d = 0.781$) aufnimmt und dadurch die Wasserschicht immer leichter wird, sodass endlich ihr spezifisches Gewicht kleiner als das von Benzol ($d = 0.881$) wird, wodurch ein Platzwechsel beider Schichten stattfindet.

(3) Inzwischen wird natürlich die Dichte der Benzolschicht durch Alkoholaufnahme abnehmen, aber dieses scheint viel langsamer vor sich zu gehen als die Dichteabnahme der Wasserschicht.

(4) Nachdem der Platzwechsel geschehen ist, nimmt die Wasserschicht an Volumen plötzlich stark zu durch sehr wenig Alkoholzusatz,

wobei das System bläulich opaleszierendes, kolloides Verhalten zeigt, welches besonders bei Abb. 3 und 4 mit verhältnismässig wasserarmen System deutlich bemerkbar ist. In dieser Gegend scheint das Wasser sein Vermögen an Alkoholaufnahme schon erschöpft zu haben. So kann die Zusammensetzung der Schichten vielleicht bei der Oberschicht alkohol- und benzolreich und bei der Unterschicht alkohol- und wasserreich sein, und das System teilt sich durch die kritische Grenzflächenspannung zwischen Benzol und Wasser in zwei Schichten. Nach einer winzigsten Zunahme von Alkohol scheint das Wasser diese Spannung zu verlieren, und das System wird homogen, d. h. molekular. Inzwischen muss das System die kolloiden Dimensionen durchlaufen, wie Wo. Ostwald[13] u. a. schon erklärt hat.

(5) Daraus könnte man vermuten, dass das disperse System benzolreich und das Dispersionsmittel ein Gemisch von Alkohol, Benzol und Wasser sein müsste. Die Bedingungen, unter welchen ein kritisches dreiflüssiges Gemisch eine stabile kolloide Emulsion angibt, sind noch zu untersuchen, aber dass sie einigermassen mit der chemischen Struktur der Komponente in wichtiger Beziehung stehen, haben wir schon bei den vorläufigen qualitativen Untersuchungen bemerkt. (Siehe Tabelle 1).

Die weiteren Untersuchungen in dieser Richtung sind bereits im Gang, ebenso wie die kolloidchemischen Untersuchungen, wie z. B. Strukturviscosität, kolloid-optische Eigenschaften u.s.w. genannter Systeme.

Zusammenfassung.

(1) Die kritischen Gemische dreier Flüssigkeiten sind auf ihr kolloides Verhalten hin studiert.

(2) Es wurde gezeigt, dass einige Systeme stabile bläulich opaleszierende, emulsoide Suspension in bestimmtem Bereich der Zusammensetzungen bei ziemlich grossem Temperaturintervall von mehr als 10 Grad angeben.

(3) System Wasser-Benzol und Äthyl- bzw. Methylalkohol hat das beste Resultat ergeben.

(4) Normal Hexan oder Pentan, die Kettenstruktur besitzen, an Stelle von Benzol ergeben negative Resultate. Daraus wurde vermutet, dass diese Erscheinung mit der chemischen Struktur der Komponente in Zusammenhang steht.

---

(13) Wo. Ostwald, *loc. cit.*

(5) Das negative Resultat mit Aceton statt Alkohol scheint auch diese Vermutung zu bestätigen.

(6) Die Verteilung von Alkohol zwischen Benzol- und Wasserschicht wurde gemessen und bestätigt, dass der grösste Teil des Alkoholzusatzes zur Wasserschicht aufgenommen wurde.

(7) Von den oben ausgeführten Untersuchungen wurde konstatiert, dass dieses bläulich opaleszierende System eine emulsoide Suspension ist, deren Dispersionsmittel alkohol- und wasserreiche Zusammensetzung aufweist und deren disperse Phase benzolreiche Zusammensetzung besitzt.

Schiomi Institut für Physikalische und Chemische Forschungen.

ON THE FADING OF DYESTUFFS. I. PHOTOCHEMICAL DECOMPOSITION OF MALACHITE GREEN AND CRYSTAL VIOLET.

By **Kenji IWAMOTO.**

Received May 29th, 1935. Published September 28th, 1935.

Although it has long been known that dyed fabrics are decolourised by the action of light, it is only quite recently that this phenomenon has been studied chemically. The phenomenon has been accounted for by several authors as oxidation, reduction, or photochemical reaction, according to the varieties of colouring matter used.

The research on this subject is very difficult, owing to the influence dependent on the following factors: (1) light source, namely intensity and wave-length of acting rays, (2) surrounding atmosphere, (3) temperature, (4) added reagents, and (5) varieties of fibres. The mechanism of fading would be qualitatively inferred from the standpoint of organic chemistry, if the decomposition products could be isolated and their constitutions determined exactly. However, our knowledge on this line is still too meagre to permit of generalisation.

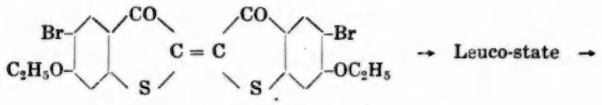
Seyewetz and Mounier[1] found that textiles of animal or vegitable fibres impregnated with nitrophenols or nitroamines turn brown by day-

(1) *Bull. soc. chim.*, (4), **43** (1928), 648.

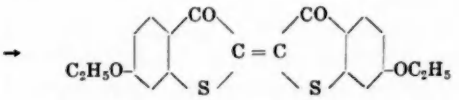
light or ultraviolet rays instead of being decolourised as other dyestuffs, owing to the probable formation of hydroxyazo-compounds.

Hibbert[2] exposed pieces of calico dyed with Indigo to sunlight or ultraviolet rays and isolated a yellow powder, m.p. 200°. This substance gave an indophenine reaction and was identified as isatin. Since isatin is also produced by the action of potassium permanganate and sulphuric acid on the same fabric, it appears that the fading of Indigo is due to the formation of isatin by its oxidation. A similar result was again observed by Haller and Ziersch[3] separately. Hibbert also obtained phthalic acid from Purpurine (1,2,4-trihydroxy-anthraquinone) and proved that the reaction was due to oxidation.

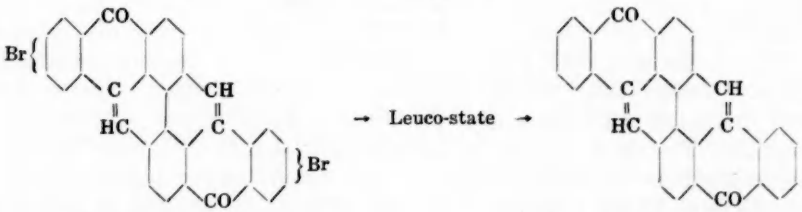
Weber[4] stated that when viscose rayon was exposed to sunlight in a dye-house, while being dyed with Helindone Fast Scarlet R, orange stripes, due to the formation of Helindone Orange R, appeared. Similarly, Indanthrene Gold Orange 4R, belonging to anthraquinone vat dyes, was changed into Indanthrene Gold Orange G:



Helindone Fast Scarlet R



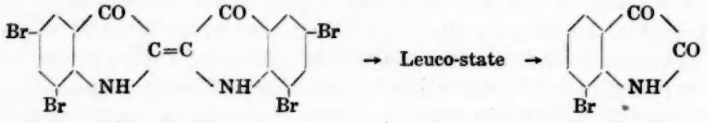
Helindone Orange R.



Indanthrene Gold Orange 4R — Indanthrene Gold Orange G.

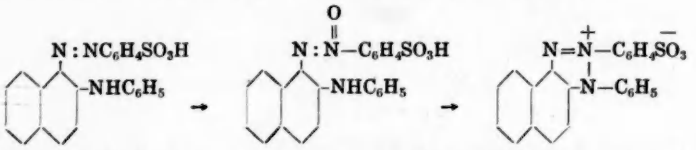
(2) *J. Soc. Dyers Colour.*, **43** (1927), 292; *ibid.*, **44** (1928), 377.
(3) *Melliand Textilberichte*, **10** (1929), 951.
(4) *Rayon Record*, **7** (1933), 227; *Am. Dyestuff Rep.*, **22** (1933), 157.

In other words, if halogen atoms are introduced into the benzene nuclei of vat dyes, the dyes are made very labile in the leuco-state to the light. In some special cases, Brilliant Indigo 4B undergoes not only dehalogenation, but also oxidation, and bromoisatin is formed:



Brilliant Indigo 4B — Bromoisatin.

Krollpfeiffer, Mühlhausen and Wolf[5] studied the action of light on azo-dyestuffs and found that aryl-β-naphthylaminoazobenzene sulphonic acid gives rise to triazonium compound on exposure to light. This change may also be accounted for by the formation of azoxy-compound and subsequent conversion of the latter into triazonium compound. In this case, the oxidation was considered to be the most important:



Phenyl-β-naphthylaminoazobenzene sulphonic acid — Azoxy-compound — Triazonium compound.

So far as we are aware, no definite compound appears to have been isolated in the decolourisation of triphenylmethane dyestuffs. Therefore, the present author has synthesised some pure dyestuffs and studied their decomposition products. In order to simplify the conditions of experiment, the powdered dyestuffs were spread in a thin layer in a large glass dish, covered with Vita-glass or cellophane paper, and exposed to direct sunlight with occasional stirring. In this manner, Malachite Green (oxalate) was rapidly changed into brown powder. The product was extracted with ether and the ethereal solution was evaporated to dryness. The faint, yellow crystals, melting at 90.5–91°, were identified as *p*-dimethylaminobenzophenone by the mixed melting point method.

Crystal Violet (oxalate) was then exposed to sunlight in the same manner, and the pale yellow crystals thus obtained, m. p. 173–174°, were identified as Michler's ketone by comparison with the pure synthetical substance. On the other hand, Georgievices[6] isolated the same ketone

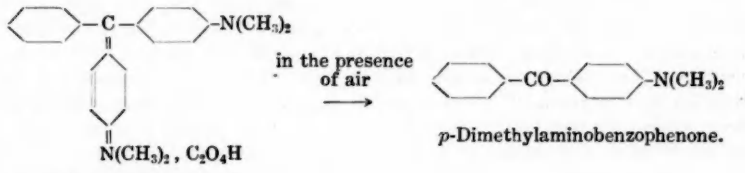
(5) *Ann.*, **508** (1933), 39.
(6) *Ber.*, **38** (1905), 886.

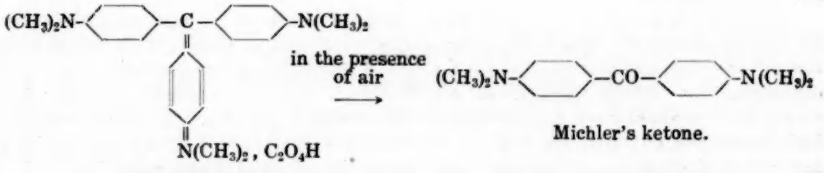
by treating a cold aqueous solution of Crystal Violet with hydrogen peroxide and ammonia. The formation of benzophenone derivatives is interpreted as being caused by either oxidation or hydrolysis.

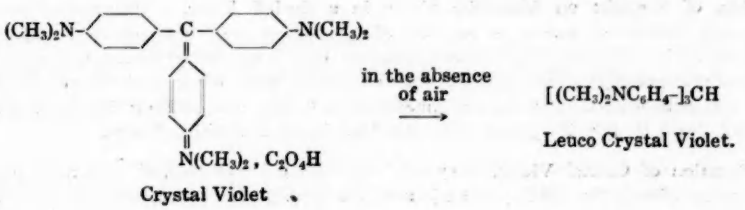
In order to ascertain whether these reactions are due to oxidation or hydrolysis, the present author exposed the same dyestuffs in a sealed tube to sunlight.

The product obtained from Malachite Green was extracted with ether. Nothing definite could be isolated from the ethereal solution, perhaps owing to the presence of impurity and to the small quantity of the material used. Nevertheless, the properties of the residue from the ethereal solution resembled leuco Malachite Green.

A grey substance from Crystal Violet was extracted with benzene and the colourless crystals, melting at 173–174°, which, on standing in the air, coloured blue gradually, were obtained and proved to be identical with leuco Crystal Violet by means of the mixed melting point method. It thus follows that the reduction occurs in this case, as shown in the following scheme:







It will be seen from the above facts that oxidation took place actually in the case where photochemical reaction might be expected. Therefore, it may be said that oxidation plays an important part in the fading of dyestuffs of this class.

Further experiment on the same line is now in progress.

Experimental.

Purification of Malachite Green. Commercial Malachite Green (50 g.) was powdered and treated with concentrated ammonia (100 c.c.) in a mortar, when the whole became colourless and the amino-base was deposited. This was collected, washed well with water, and dried. After three crystallisations from ligroin, it separated in colourless crystals which melted at 138°. The amino-base thus purified (10 g.) was dissolved by boiling with a solution of 8 g. of oxalic acid in 100 c.c. of water, when a blue solution was obtained, which was filtered. On cooling the filtrate, the small crystals of Malachite Green oxalate separated out. This was collected and recrystallised from water, when it separated in small scales and was used for next experiment without further purification.

Action of Sunlight on Malachite Green in the Air. The dye thus purified (2 g.) was ground in a mortar, spread in a Petri glass dish in a thin layer, covered with Vita-glass made by Tokyo Electric Company, and exposed to direct sunlight for about two months in autumn, when it was decomposed and changed into a dark brown powder. The product, amounting to 1.7 g., was extracted with ether and the ethereal solution was evaporated. The greenish crystals (0.54 g.) were recrystallised once from ether and then twice from dilute alcohol, from which they separated in faint, yellow crystals and melted at 90.5–91°. The melting point was unaltered by admixture with an authentic specimen of *p*-dimethylaminobenzophenone. Therefore, there can be no doubt that the substance, melting at 90.5–91°, is identical with *p*-dimethylaminobenzophenone.

For the identification of the above-mentioned substance, *p*-dimethylaminobenzophenone $(CH_3)_2NC_6H_4COC_6H_5$ was synthesised by a method described in the description of the German patent No. 41751. To a mixture of benzanilide (10 g.) and dimethylaniline (20 g.), phosphorus oxychloride (10 g.) was added and the whole was heated gradually on a water-bath with vigorous stirring. After the reaction had ceased, the oily product, $C_6H_5C(:NC_6H_5)C_6H_4N(CH_3)_2$, was hydrolysed by heating with hydrochloric acid. After being recrystallised from dilute alcohol, it melted at 90–91°.

Action of Sunlight on Malachite Green in a Sealed Tube. Malachite Green (0.5 g.) was powdered, sealed in a tube of Vita-glass, and exposed to sunlight. After a month's exposure, the contents became pale and the pressure inside the tube increased greatly. The product was extracted with ether and the ethereal solution was evaporated. The residue amounted to 0.11 g. and nothing definite could be isolated from it, but its properties resembled leuco Malachite Green.

Purification of Crystal Violet. Crystal Violet (50 g.) was treated with a 10 per cent. solution of caustic soda (200 c.c.) and the precipitate was collected, washed

well with water, and dried. This was recrystallised three times from benzene, when it separated in colourless crystals, m.p. 194°. The pure hydroxy-base was changed into a coloured oxalate by boiling with an oxalic acid solution and it was purified further by recrystallisation from hot water.

Action of Sunlight on Crystal Violet in the Air. The oxalate (2 g.) was spread in a Petri dish, covered with a plate of Vita-glass, and exposed to sunlight for two months. The grey powder thus obtained was extracted with benzene and the benzene solution was evaporated, when blue crystals (1.18 g.) were obtained. They were dissolved in dilute hydrochloric acid and filtered. The filtrate was treated with ammonia. The precipitate thus obtained was collected, washed, and dried. The yield was 0.93 g. It was recrystallised from alcohol, when it separated in yellow crystals melting at 173–174°. No lowering of the melting point was caused by admixture with the synthetic specimen of Michler's ketone, m.p. 173–174°.

Action of Sunlight on Crystal Violet in a Sealed Tube. The coloured oxalate (1 g.) was sealed in a tube of thin Vita-glass and exposed to sunlight for a month. The product was extracted with benzene and, after evaporating off the benzene from the solution, the residue (0.26 g.) was recrystallised three times from alcohol, from which it separated in almost colourless scales melting at 172–173°. For the sake of comparison, leuco Crystal Violet was prepared by the reduction of Crystal Violet and it melted at the same temperature as the decomposition product. The melting point was not depressed when mixed with pure leuco Crystal Violet.

Laboratory of Dye-Chemistry,
Kiriu Higher Technical School.

THE CONSTITUTION OF THE DIHYDROXY-DERIVATIVE OF DIPHENYLENE OXIDE OBTAINED FROM RESORCINOL.

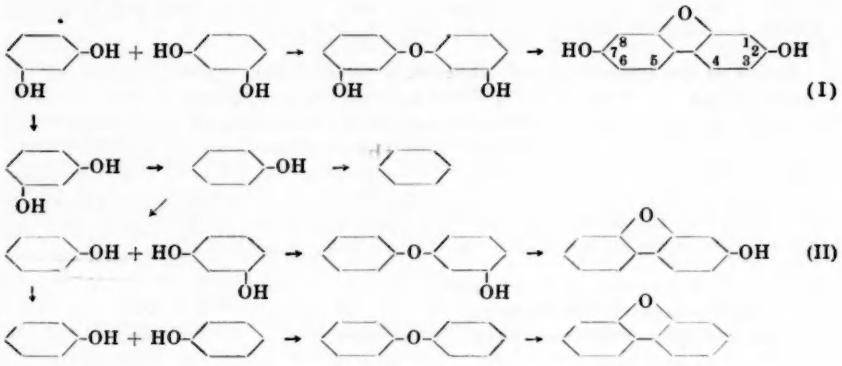
By **Kazuo HATA, Kiyoharu TATEMATSU, and Bennosuke KUBOTA.**

Received May 31st, 1935. Published September 28th, 1935.

It was previously reported[1] that resorcinol vapour, being passed over the blue oxide of tungsten at 500–550°, undergoes a certain reduction and condensation, and gives two substances besides benzene, phenol

(1) B. Kubota, Y. Fujimura, and K. Akashi, *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **2** (1925), 185; Y. Tsuzuki, *ibid.*, **6** (1927), 301.

and diphenylene oxide. These two substances, one melting at 138–138.5° and the other at 241–242°, were supposed to be monohydroxy- and dihydroxy-derivatives of diphenylene oxide respectively. In the preceding report,[2] we decided that the substance melting at 138–138.5° is 2-hydroxy-diphenylene oxide(II) by synthesizing it from 2-amino-diphenylene oxide, and considered that the substance melting at 241–242° is most probably 2,7-dihydroxy-diphenylene oxide(I). The mechanism of the reactions giving these compounds by the catalytic action of the blue oxide of tungsten, was assumed to be represented by the scheme shown below:



With the view of ascertaining the constitution of the substance melting at 241–242° we have synthesized 2,7-dihydroxy-diphenylene oxide from *p*-anisidine, and compared it with dihydroxy-diphenylene oxide obtained from resorcinol by the catalytic reaction.

The 2,7-dihydroxy-diphenylene oxide obtained from *p*-anisidine melts at 241–241.5°, and when it is mixed with the substance melting at 241–242° obtained from resorcinol, no depression of melting point can be recognized. The melting points of dimethyl derivatives of these compounds, one obtained by synthesis and the other by catalytic reaction, also coincide with each other. The melting points of these compounds are compared in Table 1.

It can be consequently decided that the substance melting at 241–242°, obtained from resorcinol, is nothing but 2,7-dihydroxy-diphenylene oxide, and that, as we have expected, the reaction follows the process represented by the scheme shown above to produce (I).

(2) K. Tatematsu and B. Kubota, This Bulletin, **9** (1934), 448.

Table 1. Comparison of the Melting Points.

Substance	From resorcinol	From *p*-anisidine	Mixed m.p.
Dihydroxy-diphenylene oxide	241–242°	241–241.5°	241–242°
Dimethoxy-diphenylene oxide	150°[3]	150°	—

Moreover, the ferric chloride reaction and the absorption curve of the synthesized 2,7-dihydroxy-diphenylene oxide quite coincide with those of the dihydroxy-diphenylene oxide obtained from resorcinol, indicating that these two substances are undoubtedly identical.

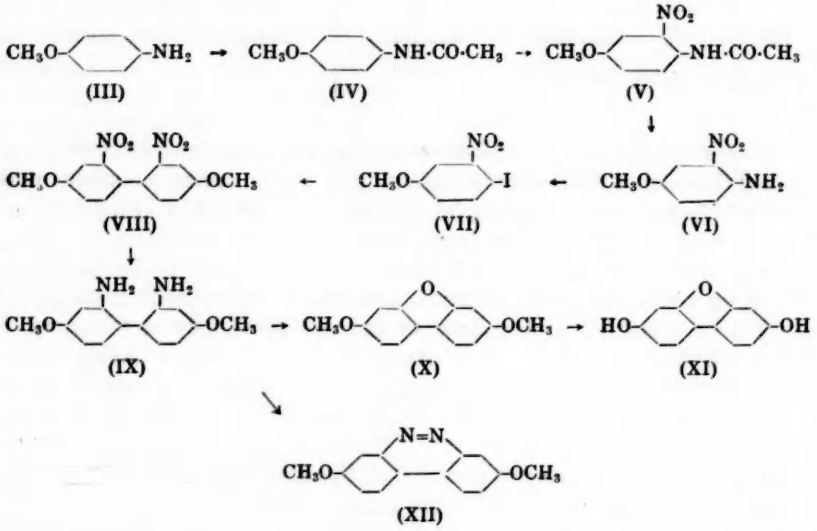
The absorption curve of 2,7-dihydroxy-diphenylene oxide, as shown by the figure in the experimental part, has a remarkable resemblance in form to those of diphenylene oxide and previously synthesized 2-hydroxy-diphenylene oxide. Further, the hydroxyl-groups having bathochromic influence on the absorption spectra, the absorption band is transferred to long wave in proportion to the number of substituted hydroxyl groups.

From these facts we can assert that the dihydroxy-diphenylene oxide melting at 241–242° obtained by the catalytic dehydration and condensation from resorcinol, has the constitution of (I) in the scheme shown above.

2,7-Dihydroxy-diphenylene oxide was synthesized as follows: *p*-anisidine(III) was changed into *p*-acetanisidide(IV) by acetylation, and after a nitro-group was introduced with nitric acid, nitro-*p*-anisidine was obtained by deacetylation,[4] which was already confirmed by H. Hähle[5] to be *o*-nitro-*p*-anisidine(VI). It was converted into *m*-nitro-*p*-iodo-anisol(VII) by the diazo-reaction, which was condensed to 2,2′-dinitro-4,4′-dimethoxy-diphenyl(VIII) with copper bronze by means of F. Ullmann's method.[6] Then it was reduced with stannous chloride and hydrochloric acid to 2,2′-diamino-4,4′-dimethoxy-diphenyl(IX). Applying E. Täuber's method of diphenylene oxide synthesis,[7] this amine was diazotized and the resulted diazonium solution was dropped into boiling copper sulphate solution, when a condensation took place giving

(3) Y. Tsuzuki, *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **6** (1927), 305.
(4) F. Reverdin, *Ber.*, **29** (1896), 2595.
(5) H. Hähle, *J. prakt. Chem.* [2], **43** (1891), 66, 67.
(6) F. Ullmann and J. Bielecki, *Ber.*, **34** (1901), 2174.
(7) E. Täuber and E. Halberstadt, *Ber.*, **25** (1892), 2745.

2,7-dimethoxy-diphenylene oxide(X). Now, by the action of hydroiodic acid, the methyl groups were removed and 2,7-dihydroxy-diphenylene oxide(XI) was obtained.

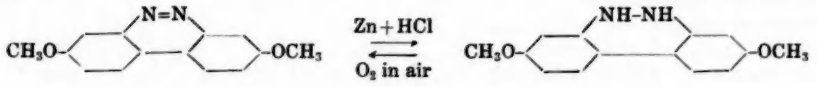


On cooling the mother liquor, from which 2,7-dimethoxy-diphenylene oxide was distilled off with steam, a new substance melting at 197° was obtained. By the investigation of its properties it was found to be 2,7-dimethoxy-phenazone(XII).

This substance separated out in dark yellow needles from water. It turned reddish brown with dilute acid, and again dark yellow when the solution was made alkaline. These colour changes were probably due to the formation and hydrolysis of phenazone salt, phenazone being a weak base. 2,7-Dimethoxy-phenazone was heated with 8% hydrochloric acid to an orange-red solution. On adding zinc dust, the solution immediately turned pale yellow, and subsequently almost colourless; it was supposed that 2,7-dimethoxy-phenazone was reduced to 2,7-dimethoxy-9,10-dihydrophenazone, similarly as phenazone was to dihydrophenazone,[8] and that the elimination of the azo group led to the decoloration. The dihydro-compound, however, was so unstable that, by removing the reducing agent, the decolourized solution soon became yellow; that is, 2,7-

(8) E. Täuber, *Ber.*, **24** (1891), 3086.

dimethoxy-phenazone was supposed to be reproduced by oxidation with air.



Now, J. J. Dobbie and his co-workers[9] reported that, main products of the reaction between the diazonium bromide of 2,2′-diamino-diphenyl and cuprous bromide, were phenazone and carbazole, while only trace of 2,2′-dibromo-diphenyl was obtained. Thereupon, it can be affirmed by this that the above-mentioned substance, melting at 197°, is 2,7-dimethoxy-phenazone. Further, it can be assumed that the black resinous matter which remained in the flask after the steam distillation, presumably contains some 2,7-dimethoxy-carbazole, but an attempt to extract this carbazole derivative was not especially made.

Experimental.

(1) **o-Nitro-p-anisidine.** (i) *p-Acetanisidide* (IV). *p*-Anisidine (25 g.) was warmed with water (30 c.c.) to form an emulsion, and acetic anhydride (20 c.c.) was added with stirring. The reaction took place at once with considerable heat evolution. After cooling, the yielded crystals were collected, and recrystallized from hot water, when colourless plates melting at 127.0–127.5° were obtained. (Yield 28 g.).

(ii) *o-Ntiro-p-acetanisidide* (V). According to F. Reverdin,[10] *p*-acetanisidide (38 g.) was mixed with 150 c.c. of 11% nitric acid, and the mixture was gradually heated to boiling. Heating was interrupted when the mixture about began to boil, and boiling continued for a while by the reaction heat. When the reaction mixture was left to cool, brown oil separated out which solidified to crystalline mass after cooling, and at the same time, some yellow needles separated out in the liquid. These were collected together, and recrystallized from water over again, yellow needles melting at 117°. (Yield 19 g.).

(iii) *o-Nitro-p-anisidine* (VI). *o*-Nitro-*p*-acetanisidide (19 g.) was heated with alcoholic potash (110 c.c.) on the water-bath under a reflux condenser. The saponification was completed after one hour. Then the solution was concentrated to about 30 c.c. and a sufficient quantity of water (50 c.c.) was added. Brilliant red crystals separated out at once, these were collected after cooling, and recrystallized from dilute alcohol to obtain red plates melting at 122.5–123.0° (Yield 14.5 g.).

(2) **m-Nitro-p-iodo-anisol** (VII). *o*-Nitro-*p*-anisidine (13.5 g.) was converted into its sulphate by heating with dilute sulphuric acid (200 c.c. of water and 9.2 c.c. of conc. sulphuric acid). Some insoluble matter was filtered off while still hot, and much quantity of sulphate separated out from the filtrate after cooling. The sulphate

(9) J. J. Dobbie, J. J. Fox, and A. J. Hoffmeister Gauge, *J. Chem. Soc.*, **99** (1911), 1615.

(10) F. Reverdin, *loc. cit.*

was collected, and the mother liquor was boiled with the previous insoluble matter to obtain more sulphate. This procedure was repeated again and again, and all the amine was converted into its sulphate. Then the sulphate was cooled below 10° together with the last mother liquor, and the solution of sodium nitrite (6.5 g. in 20 c.c. of water) was added drop by drop. Being kept for two hours, all the sulphate was diazotized to form yellow solution. It was cooled below 10°, and the potassium iodide solution (20 g. potassium iodide dissolved in 20 c.c. of water) was added drop by drop, when at once nitrogen gas was evolved vigorously, the reaction liquid turning deep black and giving iodine odour. After a while black oil separated out which solidified to a crystalline mass as it was cooled. It was allowed to stand overnight at ordinary temperature, then the black crystals were collected and washed with sodium thiosulphate solution again and again, when the black colour of iodine was easily removed and yellow crystals were obtained. After washed with 5% caustic soda solution and water, they were recrystallized from alcohol, yellow prisms[11] melting at 62°. (Yield 17.5 g.).

(3) **2,2'-Dinitro-4,4'-dimethoxy-diphenyl** (VIII). *m*-Nitro-*p*-iodo-anisol (9 g.) was thoroughly mixed with copper bronze (6 g.) in a large test tube, and heated in an oil-bath with incessant stirring. When the bath-temperature reached 130°, the viscosity of the reaction liquid suddenly increased, and copper lost its lustre to turn green-tinged white, owing to the formation of copper iodide. After being kept at 130–140° for half an hour, the temperature was raised to 160–170°, and the condensation was completed by keeping at this temperature for another half an hour. After cooling the reaction product was extracted with benzene over and over again, till benzene was no more tinged yellow. All the extracts were combined and the solvent was distilled off, when yellow crystals were obtained. They were recrystallized from benzene, yellow plates[12] melting at 136–137°. (Yield 4.0 g. Found: C, 55.70, 55.14; H, 4.32, 4.24; N, 9.28%; Mol. wt. (K. Rast), 305. Calc. for $C_{14}H_{12}N_2O_6$: C, 55.24; H, 3.98; N, 9.21%; Mol. wt., 304.)

(4) **2,2'-Diamino-4,4'-dimethoxy-diphenyl** (IX). 2,2'-Dinitro-4,4'-dimethoxy-diphenyl (5.7 g.) was dissolved in a solution of stannous chloride (60 g.) in glacial acetic acid (200 c.c.) saturated with hydrogen chloride, and after being allowed to stand overnight at room temperature, this solution was heated on the water-bath for an hour. By adding an excess (2000 c.c.) of 10% caustic soda solution, the amino compound separated out in fine crystals. It was collected and dissolved in dilute hydrochlorid acid, and purified by reprecipitation with 5% caustic soda solution after insoluble impurities were filtered off. Further, it was recrystallized from dilute alcohol when it separated out in colourless plates melting at 110.5–111.0°. (Yield 3.0 g. Found: C, 68.87; H, 6.90; N, 11.32%; Mol. wt. (K. Rast), 246. Calc. for $C_{14}H_{16}N_2O_2$: C, 68.81; H, 6.60; N, 11.48%; Mol. wt., 244.)

(5) **2,7-Dimethoxy-diphenylene oxide** (X). 2,2'-Diamino-4,4'-dimethoxy-diphenyl (1.2 g.) was dissolved in dilute hydrochloric acid (100 c.c. of water and 5 c.c. of conc. hydrochloric acid) to obtain its hydrochloride. The solution was cooled with ice,

(11) F. Reverdin described *m*-nitro-*p*-iodo-anisol as red needles melting at 62°, recrystallized from benzine or alcohol (*Ber.*, **29** (1896), 2595).

(12) This substance turns orange-yellow, when it is exposed to light for a long time.

and was diazotized by dropping sodium nitrite solution (0.7 g. sodium nitrite in 5 c.c. of water) with stirring. After being kept for two hours below 5°, the diazonium solution was gradually added drop by drop to a boiling 50% copper sulphate solution (60 g. copper sulphate in 60 c.c. of water), the latter being distilled during the addition so as to keep the volume of the solution in the flask constant.[13] Together with the distilled water, colourless crystals separated out in the condenser and receiver. After all the diazonium solution was added, the distillation was continued with the addition of water, still keeping the concentration of copper sulphate constant, until no more crystals distilled. The crystalline substance in the receiver was collected, and the condenser was washed with alcohol. After the alcoholic solution was evaporated to a small volume, a white crystalline precipitate was obtained by adding water. The products were together recrystallized from dilute alcohol, when the substance separated out in small white plates melting at 150°. (Yield 0.05 g. Found: C, 73.89; H, 5. 58%; Mol. wt. (K. Rast), 230. Calc. for $C_{14}H_{12}O_3$: C, 73.65; H, 5.30%; Mol. wt., 228.).

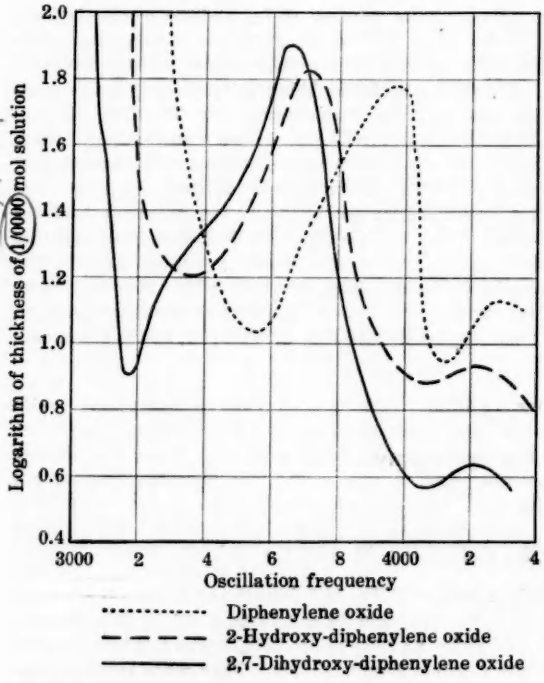
(6) **2,7-Dimethoxy-phenazone** (XII). After 2,7-dimethoxy-diphenylene oxide was thoroughly distilled off with steam, much quantity of black resinous matter in the flask was filtered off from the mother liquor while still hot. From the filtrate reddish brown needles separated out when it was cooled. It was dissolved in hot water, treated with animal charcoal, twice recrystallized from water, and dark yellow needles melting at 197° were obtained. (Yield 0.3 g. Found: N, 11.46%; Mol. wt. (K. Rast), 245. Calc. for $C_{14}H_{12}N_2O_2$: N, 11.67%; Mol. wt., 240.).

(7) **2,7-Dihydroxy-diphenylene oxide** (XI). 2,7-Dimethoxy-diphenylene oxide (50 mg.) was heated with 5 c.c. of hydroiodic acid (d = 1.7) in a sulphuric acid bath under a reflux condenser. After boiling for an hour and a half, it was left to cool after adding 10 c.c. of water, when white crystals separated out. They were collected and dissolved in dilute caustic potash solution, and reprecipitated with hydrochloric acid. Then the substance was recrystallized from hot water, some animal charcoal being used, colourless prisms melting at 241–241.5°. (Yield 12 mg.). On being dehydrated in Abderhalden's desiccating apparatus over P_2O_5 at 100° under a diminished pressure, 5.770 mg. of the substance lost 0.246 mg. of water. (Found: H_2O, 4.26. Calc. for $C_{12}H_8O_3 \cdot \frac{1}{2}H_2O$: H_2O, 4.31%.) Analysis and molecular weight determination were made with the anhydrous substance. (Found: C, 72.04; H, 4.35%; Mol. wt. (K. Rast), 204. Calc. for $C_{12}H_8O_3$: C, 71.98; H, 4.03%; Mol. wt., 200.)

2,7-Dihydroxy-diphenylene oxide thus obtained is soluble in alcohol, ether, and hot water, but scarcely soluble in cold water. When it is recrystallized from hot water, it separates out in white prisms, but being exposed to light for a long time it is gradually tinged with faint brown colour. On being heated it becomes almost colourless at 100° and melts at 241–241.5°. On adding a drop of ferric chloride solution to a solution of the substance, made by dissolving it in a very small quantity of alcohol and then adding water till the solution just begins to become turbid, it gives a green colour turning to a light brown on the addition of sodium carbonate solution.

These properties of 2,7-dihydroxy-diphenylene oxide obtained from *p*-anisidine, are perfectly coincident with those of dihydroxy-diphenylene oxide obtained from

(13) D. R. P., 167211.



resorcinol.[14] Moreover, no depression was observed in the mixed melting point of these two substances, indicating the identity of them.

Absorption curves. The absorption curve of 2,7-dihydroxy-diphenylene oxide obtained from *p*-anisidine was observed, and at the same time those of dihydroxy-diphenylene oxide obtained from resorcinol and 2-hydroxy-diphenylene oxide obtained from 2-amino-diphenylene oxide were also observed afresh. The results of their comparative study are shown in the figure, where the absorption curve of dihydroxy-diphenylene oxide obtained from resorcinol is not especially drawn as it is superposed on that of 2,7-dihydroxy-diphenylene oxide obtained from *p*-anisidine. All the observations of absorption spectra were made in a 1/10000 mol alcoholic solution.

As already pointed out, these curves strikingly resemble in form to that of diphenylene oxide,[15] suggesting that the substances melting at 138–138.5° and 241–242° obtained from resorcinol are derivatives of diphenylene oxide. It is remarkable that the absorption band removes to long wave with the increase of substituted hydroxyl groups, which have a bathochromic effect upon the absorption spectra.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

(14) Y. Tsuzuki, *Sci. Pap. Inst. Phys. Chem. Research, Japan,* **6** (1927), 304. 304.

(15) Y. Tsuzuki, *loc. cit.* K. Tatematsu and B. Kubota, *loc. cit.*

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. VII. THE SEPARATION OF HIGHLY UNSATURATED C_{22}-ACIDS.

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received June 3rd, 1935. Published September 28th, 1935.

As stated in the first report[1] of this series, the highly unsaturated acids of sardine oil contain clupanodonic acid $C_{22}H_{34}O_2$ as a most important constituent. It was first separated by Tsujimoto. Regarding its constitution there have been appeared the studies of the same author and also of Inoue and Sahashi, which will be mentioned in a succeeding paper. This acid appears to be of common occurrence in marine animal oils as an important constituent of highly unsaturated acids, since it has hitherto been found in various kinds of marine animal oils besides sardine oil. Tsujimoto and his co-workers[2] found the same acid in giebel oil, in the liver oil from *Stereolepis ischinagi*, in eel oil, cod liver oil and herring roe oil. According to Ueno and Iwai,[3] the menuke oil and the liver oil from *Scoliodon laticaudes* contain clupanodonic acid. We[4] found clupanodonic acid in several kinds of whale oils (oils from the whales belonging to Mysticete), cod liver oil, sperm oil, pilot-whale oil, and in several kinds of the liver oils from Elasmobranch fish. The majority of the oils examined by us seemed to contain, in addition to clupanodonic acid, an acid $C_{22}H_{36}O_2$, whilst there were indications of the presence of a more highly unsaturated acid $C_{22}H_{32}O_2$ in the liver oils from Elasmobranch fish. Suzuki and his co-workers[5] stated, in their studies on glycerides constituents, the separation of some glycerides containing clupanodonic acid as a fatty acid component from a number of marine animal oils, and also a glyceride containing an acid $C_{22}H_{36}O_2$ from

(1) This Bulletin, **4** (1929), 83.

(2) Tsujimoto, *Report of the Tokyo Imperial Industrial Research Laboratory*, **18** (1923), No. 2; *ibid.*, **24**(1929), No. 4; *ibid.*, **26** (1931), No. 10; Tsujimoto and Koyanagi, *ibid.*, **25** (1930), No. 4; Tsujimoto and Kimura, *J. Soc. Chem. Ind., Japan*, **26** (1923), 1162.

(3) *J. Soc. Chem. Ind., Japan*, **37** (1934), 121, 562.

(4) Toyama, *J. Soc. Chem. Ind., Japan*, **28** (1925), 95, 104; *ibid.*, **29** (1926), 531, 538, 624; *ibid.*, **30** (1927), 519; Toyama and Tsuchiya, *ibid.*, **28** (1925), 966; *ibid.*, **30** (1927), 63, 116, 207; Toyama, *Report of the Tokyo Imperial Industrial Research Laboratory*, **27** (1932), No. 2.

(5) *Proc. Imp. Acad. Japan*, **5** (1929), 265, 269.

sardine and herring oils. Brown and Beal[6] found clupanodonic acid and an acid $C_{22}H_{32}O_2$ among the highly unsaturated C_{22}-acids in menhaden, cod liver, herring, salmon and sardine oils. Recent investigations by Ono,[7] Okada,[8] and Tomiyama[9] showed clupanodonic acid to be a constituent of the oil obtained from the egg of *Squalus sucklii* and the tunny body and liver oils. Although the conclusions set forth by some of the above-mentioned authors appear not to have been supported by a sufficient experimental evidence, and although the constituents of the highly unsaturated acids are not alike, depending on the kinds of marine animal oils, it seems as a whole that sardine oil and other marine animal oils contain clupanodonic acid and some other acids, such as $C_{22}H_{32}O_2$ and $C_{22}H_{36}O_2$, as highly unsaturated C_{22}-acids. The acid $C_{22}H_{36}O_2$ has been reported to occur also in alligator oil,[10] badger fat,[11] ox liver fat,[12] and algae oil,[13] besides the marine animal oils.

The following two methods have hitherto been employed for the separation of clupanodonic acid from the marine animal oils:

(1) Bromination of the mixed fatty acids of marine animal oils and the separation of the ether-insoluble bromides give the highly unsaturated acids on subsequent debromination. Methyl esters of these acids are then fractionally distilled and a fraction corresponding to methyl clupanodonate is collected separately.

(2) A concentrated fraction of highly unsaturated acids is first prepared by means of the lithium-soap-acetone method or the sodium-soap-acetone method. This is then converted into methyl esters and the latter subjected to a fractional distillation, by which a fraction corresponding to methyl clupanodonate is collected separately.

These methods will give a good result, indeed, provided that the highly unsaturated C_{22}-acids consist almost entirely of clupanodonic acid, but when clupanodonic acid is present in association with some other highly unsaturated C_{22}-acids, such as $C_{22}H_{32}O_2$ and $C_{22}H_{36}O_2$, it seems quite difficult to separate them into individual constituents by a single application of the above methods; consequently the highly unsaturated

(6) *J. Am. Chem. Soc.*, **45** (1923), 1289.
(7) *J. Agr. Chem. Soc. Japan*, **8** (1932), 788.
(8) *Journal of the Imperial Fisheries Institute*, **28** (1932), 105.
(9) *Bulletin of the Japanese Society of Scientific Fisheries*, **2** (1933), No. 1.
(10) Kobayashi, *J. Soc. Chem. Ind., Japan*, **25** (1922), 691.
(11) Ueno and Kuzei, *J. Soc. Chem. Ind., Japan*, **29** (1926), 525.
(12) Kimura, *J. Soc. Chem. Ind., Japan*, **28** (1925), 1366.
(13) Tsujimoto, *J. Soc. Chem. Ind., Japan*, **28** (1925), 386.

C_{22}-acid which was prepared by the above methods as a clupanodonic acid can not be taken as proved to be a chemical individual. The analytical constants of additive character, such as elementary composition, neutralisation value, iodine value, alone do not furnish a criterion for the purity of the clupanodonic acid prepared by the above methods, since there may be a possibility that a mixture containing the acids $C_{22}H_{32}O_2$ and $C_{22}H_{36}O_2$ together with clupanodonic acid may show the analytical constants which agree with or, at any rate, do not deviate widely from the calculated values for clupanodonic acid. Under these considerations, we have first separated in these experiments the highly unsaturated C_{22}-acids by means of the sodium-soap-acetone method and the fractional distillation of the methyl esters, then we have subjected the highly unsaturated C_{22}-acids to a further separative method in order to effect a separation into the portions having different degrees of unsaturation. For this purpose the sodium-soap-acetone method was modified; i.e., the highly unsaturated acids were separated into more highly and less highly unsaturated portions by dissolving in acetone, partially neutralising with sodium hydroxide solution, and fractionally precipitating the sodium soaps, the amount of water and alcohol in the solvent (acetone) being made extremely small. Each portion was treated again in a similar way to effect a further separation, and after repeating this separative operation many times, we have succeeded in separating clupanodonic acid in a much purer state than was hitherto prepared. There was obtained also a fraction consisting mainly of an acid $C_{22}H_{32}O_2$ on the one hand, and a fraction having a lesser degree of unsaturation than clupanodonic acid on the other. The latter was, however, found to be contaminated with a small portion of cetoleic acid $C_{22}H_{42}O_2$ belonging to mono-ethylenic acid series. The presence of an acid $C_{22}H_{36}O_2$ could not be ascertained.

Experimental.

1. **Separation of Highly Unsaturated C_{22}-acids from Sardine Oil.** In the 4th report,[14] the methyl esters (8 kg.) of crude highly unsaturated acids were subjected to fractional distillation in order to separate the fraction consisting of the methyl esters of highly unsaturated C_{20}-acids. The higher fractions obtained thereby contained the methyl esters of highly unsaturated C_{22}-acids. At first, these fractions were worked up for the separation of highly unsaturated C_{22}-acids, but since they were found to contain some esters formed by intramolecular rearrangement, or intramolecular polymerisation, of highly unsaturated esters, further experiments on these fractions were discontinued, and another specimen of sardine oil was used as

(14) This Bulletin, **10** (1935), 241.

a starting material for the separation of highly unsaturated C_{22}-acids. Such intramolecular rearrangement, together with intermolecular polymerisation, is considered to take place during the fractional distillation when the temperature of the bath is too high.

The sardine oil used for this experiment was procured from Hokkaido and had d_4^{15} 0.9293, n_D^{15} 1.4818, acid value 2.2, saponification value 189.7, iodine value[15] 176.3, unsaponifiable matter 0.59%. The mixed fatty acids yielded 61.49% of ether-insoluble bromides.

This oil was first treated by the sodium-soap-acetone method in the following manner: 50 g. of oil was saponified with 75 c.c. of sodium hydroxide solution prepared by dissolving 50 g. of sodium hydroxide in 100 c.c. of water and 200 c.c. of 95% alcohol. After saponification, the excess of sodium hydroxide was neutralised with an acetic acid solution prepared by mixing equal volumes of glacial acetic acid and water. Denoting the number of c.c. of acetic acid solution required for neutralisation by A, 880 c.c. of acetone and $(45-A)$ c.c. of water were added to the soap solution, and the precipitate of insoluble sodium soaps was filtered. The sodium soaps remaining in the filtrate were decomposed with hydrochloric acid to obtain the free fatty acids, which consisted mainly of highly unsaturated acids and had neutralisation value 181.9 and iodine value 311.5. The yield of these fatty acids was about 4 kg. from 10 kg. of sardine oil. These were converted into methyl esters (4 kg.) which on fractionation yielded the results given in Table 1.

Table 1.

Fraction	B.p./2 mm.	Saponif. value	Iodine value	Yield (g.)
(1)	Below 170°	191.6	190.2	610
(2)	170–180°	186.4	236.8	660
(3)	180–190°	177.6	283.3	653
(4)	190–200°	170.4	325.1	744
(5)	200–214°	163.4	365.4	1180
Residue and loss	—	—	—	153

The fraction (4) yielded, on refractionation, appreciable amounts of a fraction boiling over 200°/2 mm. The latter was united with the fraction (5) and subjected to a repeated fractionation, by which a fraction (394 g.) boiling at 207–212°/2 mm. was collected separately. It had d_4^{15} 0.9247, n_D^{15} 1.4959, saponif. value 162.4, iodine value 370.8. The free acids liberated from this methyl ester fraction had d_4^{15} 0.9397, n_D^{15} 1.5039, neutr. value 170.1, iodine value 386.2, and gave 129% of ether-insoluble bromides having Br-content 71.40%. Hydrogenation of the free acids yielded behenic acid which, after recrystallisation from 95% alcohol, had neutr. value 164.5 and melted at 80.5–81° alone or admixed with a pure specimen of behenic acid. Accordingly the free acids obtained above were proved to consist of C_{22}-acids. Their

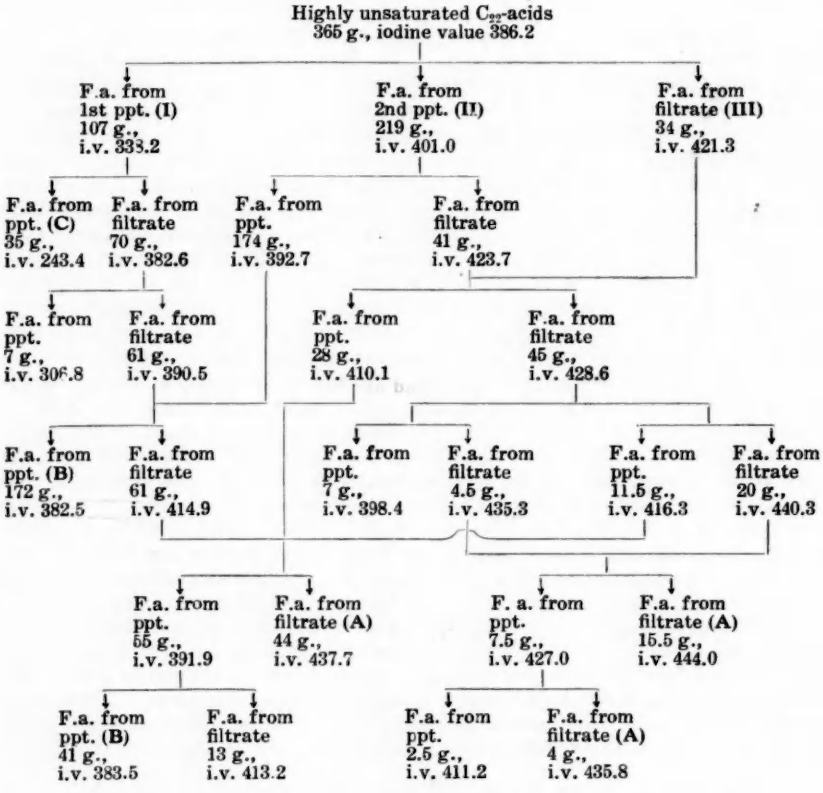
(15) Unless otherwise stated, the iodine values recorded in this paper were determined by the Wijs method.

iodine value is close to the calculated value (384.2) for clupanodonic acid $C_{22}H_{34}O_2$, but a further examination described below revealed that they contained, in addition to clupanodonic acid, an acid $C_{22}H_{32}O_2$ and some less unsaturated acids.

2. **Further Separation of Highly Unsaturated C_{22}-Acids by Means of Fractional Precipitation of their Sodium Soaps.** The highly unsaturated C_{22}-acids obtained above were separated into the fractions having different degrees of unsaturation in the following manner: 50 g. of the acids were dissolved in 1 l. of acetone and partially neutralised by using a portion of the sodium hydroxide solution prepared by dissolving 50 g. of sodium hydroxide in 100 c.c. of water and 200 c.c. of 95% alcohol. After the precipitate of sodium soaps was once brought into the solution by warming on the water-bath, the solution was allowed to cool to reprecipitate the insoluble sodium soaps which were collected, and on acidification there were obtained the fatty acids (I). The fatty acids remaining in the filtrate were once recovered and dissolved again in acetone, partially neutralised as before and the precipitated sodium soaps on acidification gave the fatty acids (II). The filtrate contained the fatty acids (III) of highest unsaturation which were recovered in the usual way. The fatty acids thus obtained (I, II, and III) were subjected to a further separation by dissolving in a little acetone, partially neutralising by using a portion of the sodium hydroxide solution prepared by dissolving 50 g. of sodium hydroxide in 50 c.c. of water and 100 c.c. of 95% alcohol, and adding more acetone so as to precipitate the insoluble sodium soaps. On decomposing the latter with hydrochloric acid, the fatty acids of comparatively low unsaturation were obtained, whereas the filtrate yielded the remaining fatty acids of highest unsaturation. For every 100 g. of the fatty acids, about 2 l. of acetone was used in most cases; but the quantity of acetone was somewhat changed depending upon the quantity of sodium hydroxide solution used for the partial neutralisation. In short, this method of separation is based upon the fact that the solubility of the sodium soaps of highly unsaturated acids in acetone containing water or alcohol increases with the degree of unsaturation of the highly unsaturated acids. Since the solubility of the sodium soap of a highly unsaturated acid decreases with the decrease in water or alcohol content in acetone and this effect is remarkably high, caution must be taken to determine the purity of acetone when the recovered acetone is used for this purpose. After repeating this separative operation, there were obtained the results given in Table 2.

3. **Separation of a Concentrated Fraction of Docosahexenoic Acid $C_{22}H_{32}O_2$.** It appears from the iodine values that the fractions (A) recorded in Table 2 contain a large amount of docosahexenoic acid $C_{22}H_{32}O_2$. These were combined, and subjected to a fractional precipitation of sodium soaps in acetone. The less unsaturated portion was removed as the precipitate of insoluble sodium soaps. The more unsaturated portion recovered from the filtrate was treated again as before in order to obtain the still more unsaturated portion by removing a further quantity of less unsaturated portion, and after this separative operation had been repeated several times, there was obtained finally a fatty acid fraction of the highest unsaturation which was deemed to consist largely of docosahexenoic acid together with a little clupanodonic acid. It had the following constants: d_4^{15} 0.9521, d_4^{20} 0.9486, n_D^{15} 1.5129, n_D^{20} 1.5109, neutralisation value 170.1, iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 456.0 and 440.8 respectively (calc. for $C_{22}H_{32}O_2$: neutr. value 170.9, iodine value 464.0), thiocyanogen value 225.7 (calc. for the formation of hexathiocyanate:

Table 2.

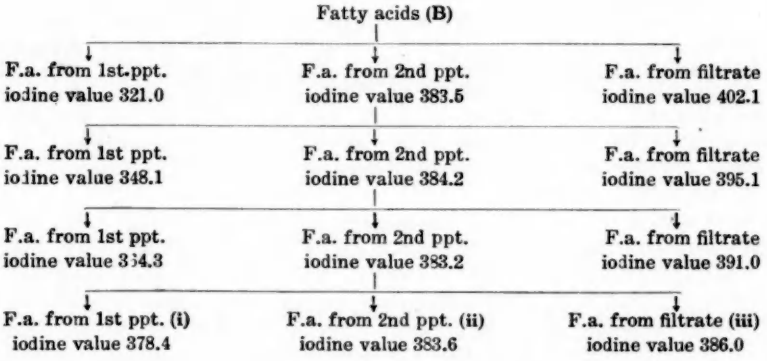

Highly unsaturated C_{22}-acids
365 g., iodine value 386.2
F.a. from 1st ppt. (I) 107 g., i.v. 333.2
F.a. from 2nd ppt. (II) 219 g., i.v. 401.0
F.a. from filtrate (III) 34 g., i.v. 421.3
F.a. from ppt. (C) 35 g., i.v. 243.4
F.a. from filtrate 70 g., i.v. 382.6
F.a. from ppt. 174 g., i.v. 392.7
F.a. from filtrate 41 g., i.v. 423.7
F.a. from ppt. 7 g., i.v. 306.8
F.a. from filtrate 61 g., i.v. 390.5
F.a. from ppt. 28 g., i.v. 410.1
F.a. from filtrate 45 g., i.v. 428.6
F.a. from ppt. (B) 172 g., i.v. 382.5
F.a. from filtrate 61 g., i.v. 414.9
F.a. from ppt. 7 g., i.v. 398.4
F.a. from filtrate 4.5 g., i.v. 435.3
F.a. from ppt. 11.5 g., i.v. 416.3
F.a. from filtrate 20 g., i.v. 440.3
F.a. from ppt. 55 g., i.v. 391.9
F.a. from filtrate (A) 44 g., i.v. 437.7
F. a. from ppt. 7.5 g., i.v. 427.0
F.a. from filtrate (A) 15.5 g., i.v. 444.0
F.a. from ppt. (B) 41 g., i.v. 383.5
F.a. from filtrate 13 g., i.v. 413.2
F.a. from ppt. 2.5 g., i.v. 411.2
F.a. from filtrate (A) 4 g., i.v. 435.8

232.0). It yielded 177% of ether-insoluble bromide which turned black at about 240° without melting (Found: Br, 74.00. Calc. for $C_{22}H_{32}O_2Br_{12}$: Br. 74.50%).

4. **Separation of Clupanodonic Acid** $C_{22}H_{34}O_2$. The fatty acid fractions (B) in Table 2 were united and dissolved in acetone, and a small amount of the sodium hydroxide solution was added so as to precipitate a small portion of the fatty acids as insoluble sodium soaps which were filtered. The filtrate was then completely neutralised with the sodium hydroxide solution and the bulk of the fatty acids was precipitated as insoluble sodium soaps. The free fatty acids were isolated from the 1st and 2nd precipitates and also from the final filtrate in the usual way. The fatty acids obtained from the 1st precipitate showed comparatively low iodine value, whilst those obtained from the final filtrate showed the highest iodine value. The fatty acids obtained from the 2nd precipitate were treated again as before in order

to separate into three portions, and after repeating this separative operation, there were obtained the results shown in Table 3.

Table 3.



The iodine values of the fatty acid fractions (i, ii, and iii) obtained by the final separation do not differ much from one another, and the fatty acid fraction (ii) seems to consist largely of clupanodonic acid, the iodine value of which is 384.2.

The fatty acid fraction (ii) was converted into methyl ester and the latter was subjected to the fractional distillation by which a fraction boiling at 207–212°/2 mm. was collected as methyl clupanodonate. It had the following constants: d_4^{15} 0.9240, d_4^{20} 0.9205, n_D^{15} 1.4955, n_D^{20} 1,4934, molecular refraction 108.8 (calc. for $C_{25}H_{36}O_2$ F 5: 107.7), saponif. value 163.0 (calc. 163.0), iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 368.0 and 353.9 respectively (calc. 368.6), thiocyanogen value 148.9 (calc. for the formation of tetrathiocyanate: 147.5).

Clupanodonic acid set free from the methyl ester showed d_4^{15} 0.9390, d_4^{20} 0.9356, n_D^{15} 1.5035, n_D^{20} 1.4934, molecular refraction 104.1 (calc. for $C_{22}H_{34}O_2$ F 5: 103.0), neutr. value 170.4 (calc. 169.8), iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 383.2 and 366.3 respectively (calc. 384.2), thiocyanogen value 155.2 (calc. for the formation of tetrathiocyanate 153.7). It yielded 156% of ether-insoluble bromide which turned black at about 240° without melting (Found: Br, 70.88. Calc. for $C_{22}H_{34}O_2Br_{10}$: Br, 70.76%).

5. **Examination of the Comparatively Less Unsaturated Fraction.** The iodine value (243.4) of the fatty acid fraction (C) in Table 2 indicates that this fraction contains some less unsaturated fatty acids than clupanodonic acid. The fraction was separated into two portions by means of fractional precipitation of sodium soaps in acetone, the less unsaturated portion obtained from the precipitate of insoluble sodium soaps was subjected to a further separation, and after repeating this separative operation, there was obtained finally a fatty acid fraction (about 5 g., iodine value 109.9) from the precipitate of insoluble sodium soaps. On cooling the solution of this fraction in 80% alcohol, a crystalline solid separated; it had neutr. value 165.0, iodine value 74.9 and m.p. 32–32.5°, and it was identified as cetoleic acid (neutr. value

165.8, iodine value 75.0, and m.p. 32.5–33°) by the mixed melting point test. It was thus ascertained that the fraction (C) contained cetoleic acid, though in a minor amount. This indicated that when the sardine oil was first treated by the sodium-soap-acetone method, a small amount of cetoleic acid remained in the acetone solution, so that it entered into the concentrated fraction of highly unsaturated acids, and became concentrated in this fraction (C) by subsequent separative operations. The filtrates which came from the separative operations on the fraction (C) yielded the fatty acid fractions having iodine values 350.8, 304.4, and 205.7 respectively, but no individual acid could be isolated from these fractions. Should the sardine oil contain an acid $C_{22}H_{36}O_2$, it would enter into the fatty acid fraction (C), but its presence in the fraction (C) could not be ascertained by this experiment, though the absence of this acid should not be prematurely concluded.[16]

Summary.

A concentrated fraction of highly unsaturated acids has been separated from sardine oil by means of sodium-soap-acetone method. It was converted into methyl esters and the latter subjected to a fractional distillation which yielded a fraction consisting of the methyl esters of C_{22}-acids. This fraction and the free fatty acids liberated from it showed iodine values which were close to those of methyl clupanodonate and clupanodonic acid respectively, but on separating the fatty acids of this fraction by a fractional precipitation of sodium soap in acetone solution, they were found to contain, in addition to clupanodonic acid, some acids of different degrees of unsaturation. After a repeated separation, clupanodonic acid has been separated in much purer state than prepared hitherto, and also a more highly unsaturated portion consisting chiefly of docosahexenoic acid $C_{22}H_{32}O_2$ has been separated. There was obtained also a less unsaturated portion than clupanodonic acid; this was, however, found to be a mixture contaminated with cetoleic acid $C_{22}H_{42}O_2$, though in a minor amount. Docosatetraenoic acid $C_{22}H_{36}O_2$ was not separated, although this acid could not be altogether deemed to be absent.

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

(16) In previous studies (*loc. cit.*) on the fatty acids constituents of various kinds of marine animal oils, we have inferred the presence of an acid $C_{22}H_{36}O_2$ from the fact that in the case of the majority of the oils examined, the highly unsaturated C_{22}-acids showed an iodine value somewhat lower than the calculated value for clupanodonic acid. However, taking the results of the present investigation into consideration, the low iodine values of the highly unsaturated C_{22}-acids obtained in the previous studies might have been due to the contamination of some less unsaturated acids, such as cetoleic acid $C_{22}H_{42}O_2$, and not to the presence of the acid $C_{22}H_{36}O_2$.

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. VIII. THE CONSTITUTION OF CLUPANODONIC ACID $C_{22}H_{34}O_2$.

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received June 8th, 1935. Published September 28th, 1935.

As described in the preceding paper, we have separated from sardine oil a mixture of highly unsaturated C_{22}-acids which was resolved further into the portions of different degrees of unsaturation in order to obtain clupanodonic acid $C_{22}H_{34}O_2$ in a much purer state than prepared heretofore and also a more highly unsaturated fraction consisting chiefly of docosahexenoic acid $C_{22}H_{32}O_2$. The present paper deals with the constitution of clupanodonic acid. The same subject has hitherto been studied by Tsujimoto[1] and also by Inoue and Sahashi.[2] On subjecting clupanodonic acid and its amyl ester to ozonolysis, Tsujimoto found propyl aldehyde, acetaldehyde, carbon dioxide together with comparatively large quantities of succinic acid, and also amyl hydrogen succinate in the case of amyl clupanodonate. Since acetaldehyde and carbon dioxide were considered to be formed by a further degradation of malonic aldehyde, the above results indicated that clupanodonic acid had the following groups: $CH_3{\cdot}CH_2{\cdot}CH=$, $=CH{\cdot}CH_2{\cdot}CH=$, $=CH{\cdot}(CH_2)_2{\cdot}CH=$ and $=CH{\cdot}(CH_2)_2{\cdot}COOH$, of which it had three of the group $=CH{\cdot}(CH_2)_2{\cdot}CH=$. In regard to the respective positions of the groups $=CH{\cdot}CH_2{\cdot}CH=$ and $=CH{\cdot}(CH_2)_2{\cdot}CH=$, he showed no experimental evidence, but he assumed clupanodonic acid to have one of the ethylenic linkings in the same position as cetoleic acid ($\Delta^{11:12}$-docosenoic acid) which is found to occur widely in marine animal oils, and ascribed to clupanodonic acid the following alternative formulae:

$CH_3{\cdot}CH_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}CH_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}COOH$
or
$CH_3{\cdot}CH_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}CH_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}COOH.$

By oxidation of clupanodonic acid with potassium permanganate in acetone, Inoue and Sahashi obtained butyric, pimelic, succinic, adipic,

(1) This Bulletin, **3** (1928), 299.
(2) *Proc. Imp. Acad. Japan*, **8** (1932), 371.

malonic and oxalic acids, of which adipic and oxalic acids were assumed to have been formed by the secondary decomposition of pimelic and malonic acids respectively, and taking the yields of these oxidation products into consideration, they concluded that clupanodonic acid yielded butyric, pimelic, succinic (2 mols) and malonic acids as scission products derived from the respective groups jointed by the unsaturated linkings. In order to determine in what order the respective groups are jointed, these authors subjected clupanodonic acid to a partial hydrogenation, separated the hydrogenation products into the fractions of different degrees of saturation and examined each fraction by the permanganate oxidation with the results given in Table 1.

Table 1.

Clupanodonic acid and its partially hydrogenated products	Oxidation products (acids)				
Clupanodonic acid	Butyric, (C_4)	Pimelic, (C_7)	Succinic, (C_4)	Malonic, (C_3)	Succinic (C_4)
Partially hydrogenated products					
Fraction which yields a hexabromide	Undecanoic, (C_{11})		Succinic, (C_4)	Malonic, (C_3)	Succinic (C_4)
Fraction which yields a tetrabromide	Pentadecanoic, (C_{15})			Malonic, (C_3)	Succinic (C_4)
Fraction which yields a dibromide	Stearic, (C_{18})				Succinic (C_4)

Based on these results Inoue and Sahashi ascribed to clupanodonic acid the following formula having one triple and three double linkings:

$$CH_3\cdot(CH_2)_2\cdot C\equiv C\cdot(CH_2)_5\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH.$$

It is to be noted that the samples of clupanodonic acid used in the experiments of Tsujimoto and the subsequent authors were prepared by means of the lithium-soap-acetone method and the fractional distillation of methyl esters without applying a further separative operation, consequently they must have been contaminated with some other acids of different degrees of unsaturation as pointed out in our previous report.

In this paper, the same sample of clupanodonic acid as described in the preceding paper was converted into the amyl ester, and the latter was subjected to ozonolysis. Among the products of ozonolysis, propyl aldehyde, acetaldehyde, carbon dioxide, succinic acid and amyl hydrogen

succinate were identified; the presence of some lower acids consisting possibly of propionic and acetic acids was also indicated. Of these compounds, propyl aldehyde is evidently derived from the group $CH_3 \cdot CH_2 \cdot CH=$, whilst acetaldehyde and carbon dioxide are attributable to the secondary decomposition of the product of ozonolysis derived from the group $=CH \cdot CH_2 \cdot CH=$. Succinic acid and amyl hydrogen succinate are derived from the groups $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot (CH_2)_2 \cdot COOC_5H_{11}$ respectively. Accordingly clupanodonic acid has the following groups: $CH_3 \cdot CH_2 \cdot CH=$, $=CH \cdot (CH_2)_2 \cdot COOH$, $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot CH_2 \cdot CH=$, of which it has three of the group $CH \cdot (CH_2)_2 \cdot CH=$, since it contains 22 carbon atoms in its molecule. These results, however, give no information regarding the respective positions of the groups $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot CH_2 \cdot CH=$, and it requires a further examination to establish the constitution of clupanodonic acid. In the case of moroctic acid ($\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16}$-octadecatetraenoic acid), we have determined the respective positions of the groups by preparing tetrathiocyanate (4,5,8,9-tetrathiocyanate) by the selective addition of thiocyanogen to methyl moroctate, and by examining this tetrathiocyanate by ozonolysis. We have, however, found by subsequent studies[3] on the partial bromination of the poly-ethylenic acids of known constitution, such as linoleic and linolenic acids, that the addition of bromine took place selectively at the specified ethylenic linkings of these poly-ethylenic acids; though such a selective addition did not proceed to a quantitative extent, the products of stepwise bromination contained in every case a definite bromide formed by the selective addition as the main constituent which could be separated by means of a suitable separative operation. After having found the above fact, we have applied this to clupanodonic acid, and determined the positions of the groups $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot CH_2 \cdot CH=$ by examining the products of partial bromination of clupanodonic acid by ozonolysis. The results are summarized below. It deserves a special attention that whilst thiocyanogen added selectively to the two ethylenic linkings which existed near the carboxyl group of moroctic acid, bromine attacked preferentially the ethylenic linkings which were further removed from the carboxyl group of clupanodonic acid.[4]

---

(3) *J. Soc. Chem. Ind., Japan*, **38** (1935), 89.

(4) The same relation was observed in the case of linoleic and linolenic acids, viz., whilst thiocyanogen attacked selectively the 9:10-ethylenic linking of linoleic acid and also the 9:10- and the 12:13-ethylenic linkings of linolenic acid, bromine attacked preferentially the ethylenic linking which was the further removed from the carboxyl group. Cf. Toyama and Tsuchiya, *J. Soc. Chem. Ind., Japan*, **38** (1935), 86, 89.

(1) Dibromo-derivative $C_{22}H_{34}O_2Br_2$ obtained by the addition of 1 mol bromine to 1 mol clupanodonic acid yielded, as the products of ozonolysis, acetaldehyde, carbon dioxide, succinic acid and an oily bromo-compound which on debromination and subsequent hydrogenation gave heptoic acid, indicating that the oily bromo-compound obtained above consisted of dibromoheptoic acid. Since clupanodonic acid was shown to contain the group $CH_3 \cdot CH_2 \cdot CH=$ by the ozonolysis of amyl clupanodonate, it follows from the above results that it contains the group $CH_3 \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=$.

(2) Tetrabromo-derivative $C_{22}H_{34}O_2Br_4$ obtained by the addition of 2 mols bromine to 1 mol clupanodonic acid yielded, as the products of ozonolysis, succinic acid and an oily bromo-compound which on debromination and subsequent hydrogenation gave capric acid. This fact, coupled with the result obtained by the ozonolysis of dibromo-derivative, indicated the presence of the group $CH_3 \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot CH_2\, CH=$.

(3) Hexabromo-derivative $C_{22}H_{34}O_2Br_6$ was prepared by the addition of 3 mols bromine to 1 mol clupanodonic acid. Ozonolysis of this bromide yielded succinic acid and an oily bromo-compound, from which myristic acid was obtained by debromination followed by hydrogenation. Hence clupanodonic acid was found to contain the group $CH_3 \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=$.

From these results the constitution of clupanodonic acid was established as follows:

$$CH_3 \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_2 \cdot COOH.$$

Comparing the results of our experiments with those obtained by Tsujimoto, they show a full agreement in that clupanodonic acid consists of the groups: $CH_3 \cdot CH_2 \cdot CH=$, $=CH \cdot (CH_2)_2 \cdot CH=$ (three), $=CH \cdot CH_2 \cdot CH=$, and $=CH \cdot (CH_2)_2 \cdot COOH$. While Tsujimoto derived two of his formulæ by assuming that clupanodonic acid had one of its ethylenic linkings in the same position as that of cetoleic acid ($\Delta^{11:12}$-dococenoic acid), the result of our further research in order to determine the positions of the respective groups, however, indicated that the above assumption of Tsujimoto was not substantiated, since clupanodonic acid, unlike cetoleic acid, had no ethylenic linking in the 11:12-position. Consequently Tsujimoto's formula should be corrected. Comparing the formula given by Inoue and Sahashi with that established by us, they show much difference with the exception that both formulæ contain the group $=CH \cdot (CH_2)_2 \cdot COOH$ at the side of the carboxyl group. Particularly,

the former is incompatible with the latter in that it contains a C_4-group at the side of the methyl group and a C_7-group in the adjascent place, having a triple linking between these two groups. The reason why these discrepancies occur is unknown to us. According to the results given by these authors, not only clupanodonic acid itself but also its hydrogenated products having one to three ethylenic linkings yielded on oxidation only the compounds corresponding just to the formula given by these authors, but it is quite difficult to understand the formation of the oxidation products found by these authors, such as undecanoic, pentadecanoic and stearic acids with the use of our formula, unless displacements of the unsaturated linkings occur in the course of hydrogenation. Although the possibility is not excluded that the permanganate oxidation method, when applied to a highly unsaturated acid like clupanodonic acid, gives rise to abnormal oxidation products which differ in the number of carbon atoms from those obtained by the ozonide method, it is rather inconceivable that such abnormal decomposition takes place also in the hydrogenated products of clupanodonic acid having one to three unsaturated linkings when the permanganate oxidation method is applied. For it has been generally accepted that the permanganate method, when applied to mono-ethylenic acids, gives a result which is consistent with that obtainable by the ozonide method, and furthermore we have examined the constitution of hiragonic acid having three ethylenic linkings by the permanganate and the ozonide methods, and have found that the both methods gave consistent results. Hence the difference of the oxidation methods alone can not account for the marked discrepancies between the results obtained by these authors and those obtained by us.[5]

It is a very remarkable fact that, as it is seen from our studies hitherto reported, the highly unsaturated acids, not only clupanodonic acid but also eicosatetraenoic, moroctic and hiragonic acids, have no ethylenic linking in the same positions as the corresponding monoethylenic acids as shown in Table 2.

(5) After the experiments given in this paper had been completed, there appeared another paper by Inoue and Kato (*Proc. Imp. Acad. Japan*, **10** (1934), 463) in which they maintained their formula having a triple linking. Also Kino (*Bull. Inst. Phys. Chem. Research, Japan*, **13** (1934), 1065) touched upon the constitution of clupanodonic acid in his studies on the polymerisation of highly unsaturated acids.

Table 2.

Number of carbon atoms	Highly unsaturated acids		Mono-ethylenic acids	
22	Clupanodonic	4:5, 8:9, 12:13, 15:16, 19:20	Cetoleic	11:12
20	Eicosatetraenoic	4:5, 8:9, 12:13, 16:17	Gadoleic	9:10
18	Moroctic	4:5, 8:9, 12:13, 15:16	Oleic	9:10
16	Hiragonic	6:7, 10:11, 14:15	Zoomaric	9:10

Judging from the relations between the constitutions of linolenic, linoleic and oleic acids found in vegetable oils, it would seem that one of the ethylenic linkings in the highly unsaturated acids in marine animal oils should be located in the same position as those in the corresponding mono-ethylenic acids. No such relation was, however, found to exist in any of the four above-mentioned highly unsaturated acids in marine animal oils. This is of much interest in connection with the mechanism of the formation of unsaturated fatty acids in living organism.

Experimental.

1. Ozonolysis of Amyl Clupanodonate. The same sample of clupanodonic acid as described in the previous paper was used in these experiments. It had d_4^{15} 0.9390, n_D^{15} 1.5035, neutralisation value 170.4 (calc. 169.8), iodine value[6] 383.2 (calc. 384.2), and gave 156% of ether insoluble bromide having Br-content 70.88% (calc. for $C_{22}H_{34}O_2Br_{10}$: 70.76%). It was heated with an equal amount of amyl alcohol containing 2.5% of hydrogen chloride on the water-bath for 1 hour, and after removing the excess of amyl alcohol and some unchanged clupanodonic acid, the amyl clupanodonate was separated. This was dissolved in chloroform, 50 c.c. being used for 5 g. of amyl clupanodonate, cooled with ice-salt, and treated with ozonised oxygen until the solution became saturated with ozone. The solvent was distilled off, and the ozonide was obtained as a light yellow syrup. Since the ozonide was highly unstable and there was a danger of explosive decomposition on undue heating, the chloroform was not thoroughly distilled off, and consequently the ozonide obtained above retained some chloroform. The yield of ozonide thus obtained was 17 g. (170%) from 10 g. of amyl clupanodonate. The theoretical yields for normal ozonide $C_{27}H_{41}O_{17}$ and ozonide peroxide $C_{27}H_{44}O_{18}$ are 159.9 and 163.9% respectively. Water (100 c.c.) was added to the ozonide, and the liquid was heated in a flask on the water-bath for 30 minutes. The flask containing the ozonide was attached by a delivery tube to other three flasks (a, b and c) which were connected in succession, the first (a)

(6) Unless otherwise stated, the iodine values recorded in this paper were determined by the Wijs method.

being filled with ice-cold water, and the second (b) and the third (c) being filled with approximately 1/3 N solution of barium hydroxide. During the heating, a current of hydrogen was passed into the flask containing the ozonide, and the volatile substances (A) formed by the decomposition of ozonide were carried over with hydrogen into the three flasks (a, b and c) where they were absorbed by water and barium hydroxide solution in succession. The decomposition products remained in the initial flask partly separated as an insoluble oil (C) from the aqueous solution. The aqueous solution was saturated with sodium chloride, and extracted with 1 l. of ether which dissolved the decomposition products (B) contained in the aqueous solution. After distilling off ether from the ethereal solution, there remained the decomposition products (B) as a reddish orange liquid. The products of ozonolysis were thus separated into three portions (A, B and C).

(i) *Volatile products* (A). The aqueous solution in the flask (a) produced a pink colouration with Schiff's reagent, and a deep blue colouration with diethylamine and sodium nitroprusside, indicating the presence of acetaldehyde. The presence of propyl aldehyde was also indicated by the smell of scatol which was recognised by heating the phenylhydrazone, prepared from the aqueous solution in the flask (a), with zinc chloride to 180°. A partial separation of these two aldehydes was effected by heating the solution in the flask (a) at about 45° in a current of carbon dioxide. The flask was connected with another flask containing ice-cold water by a delivery tube, and the volatilised substances which were carried over with carbon dioxide were collected in the latter. By these treatments, the substances, dissolved in the aqueous solution in the flask (a) were separated into the portion (a_1) which did not volatilise at 45° and the portion (a_2) which volatilised at 45°. The *p*-nitrophenylhydrazone prepared from the portion (a_1) melted at 122.5–123° after recrystallisation from 50% alcohol; it was found to consist mainly of *p*-nitrophenylhydrazone of propyl aldehyde (Found: N, 21.82. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The same derivative prepared from the portion (a_2) melted at 116–117° after recrystallisation from 50% alcohol; it was considered to be a mixture of *p*-nitrophenylhydrazones of acetaldehyde and propyl aldehyde (Found: N, 22.97. Calc. for $C_8H_9O_2N_3$: N, 23.46. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The solution in the flask (a) showed also an acid reaction and produced a deep red colouration on adding ferric chloride after neutralisation, from which the presence of acetic acid was inferred.

The barium hydroxide solution in the flask (b) was found to contain a large amount of a white precipitate which was also found in the flask (c) in a small amount. This precipitate was found to be barium carbonate, indicating that carbon dioxide was formed by the ozonolysis of amyl clupanodonate. Calculating from the quantity of barium carbonate, the yield of carbon dioxide was found to be 0.81 g. or 8.1% of amyl clupanodonate used for ozonolysis. If amyl clupanodonate has the group $=CH\cdot CH_2\cdot CH=$ and the products of ozonolysis derived from this group undergo a secondary decomposition with the formation of carbon dioxide to a quantitative extent, the yield of carbon dioxide should be 10.99% of amyl clupanodonate.

(ii) *Products obtained from the aqueous solution* (B). Yield 7.7 g. These were boiled out three times with petroleum ether, using 50 c.c. each time. The portion which remained insoluble was a reddish orange liquid with little crystalline deposit at room temperature. Oxidation of this portion with an alkaline solution of potassium permanganate and subsequent acidification yielded a product consisting

largely of a crystalline solid. This was spread on a sheet of filter paper in order to remove the liquid portion by means of absorption, and the remaining solid gave, after being washed with a little cold ether and then recrystallised from ethyl acetate, succinic acid which had neutralisation value 947.6 (calc. for $C_4H_6O_4$: 950.6) and melted at 182–183°, both alone and after admixture with a pure specimen of succinic acid. On removing the solvent from the petroleum ether extract, there remained a reddish orange liquid which on distillation gave 0.5 g. of a colourless distillate at 120–180° of the bath-temperature. The distillate thus obtained showed an acid reaction, and the silver salts prepared from it were found to be a mixture of silver acetate and silver propionate by analyses (Found for 1st crop of silver salt: Ag, 61.31. Found for 2nd crop of silver salt: Ag, 63.25. Calc. for $C_2H_3O_2Ag$: Ag, 64.64. Calc. for $C_3H_5O_2Ag$: Ag, 59.63%).

(iii) *Oily substances* (C). Yield 3.7 g. Oxidation of these substances with alkaline permanganate followed by acidification yielded an acid ester which had neutr. value 308.1 and saponif. value 595.5 and was deemed to consist mainly of amyl hydrogen succinate (calc. for $C_9H_{16}O_4$: neutr. value 298.2, saponif. value 596.5). The free acid liberated from this acid ester in the usual way yielded, after recrystallisation from ethyl acetate, a pure succinic acid having neutr. value 948.0, m.p. and mixed m.p. 182–183°.

2. **Ozonolysis of Dibromo-derivative of Clupanodonic Acid.** For the preparation of the dibromo-derivative of clupanodonic acid, 15 g. of the acid was dissolved in 150 c.c. of ether, cooled with ice-salt, and the bromine solution prepared by dissolving 7.5 g. (calc. for the formation of dibromo-derivative: 7.26 g.) of bromine in 15 c.c. of glacial acetic acid was gradually added with constant stirring. After all the bromine solution has been added, the ethereal solution was allowed to stand for 2 hours. No insoluble bromide separated. The ethereal solution was washed with water, then dehydrated, and on distilling off the ether, there remained 22 g. of oily bromides. These were dissolved in 10 volumes of alcohol, and fractionally precipitated by adding a little water in each time. The yield and the iodine value of each precipitate are given in Table 3.

Table 3.

Precipitate	Yield (g.)	Iodine value
1st ppt.	1.5	120.7
2nd ppt.	12	209.2
3rd ppt.	3	209.8
Bromide remaining in the final filtrate	4	230.5

The 2nd and 3rd precipitates were united and dissolved in alcohol, and after fractional precipitation as before, the dibromo-derivative was finally obtained as an oily substance which showed iodine value 208.7 (calc. for $C_{22}H_{34}O_2Br_2$: 207.2). The dibromide (10.5 g.) thus obtained was ozonised in a chloroform solution. The resulting ozonide was decomposed by heating with water in the usual way. The volatile decomposition products (A) formed were passed through the water in the flask (a) and then through the barium hydroxide solution in the two flasks (b and c) in succession. The decomposition products, which did not volatilise, partly dissolved

in water and oily substances (C) separated under the aqueous layer. The latter was thoroughly extracted with ether, and the ethereal extract yielded, on distilling off the ether, the decomposition products (B) initially dissolved in water.

(i) *Volatile decomposition products* (A). The aqueous solution in the flask (a) gives a deep blue colouration with diethylamine and sodium nitroprusside, indicating the presence of acetaldehyde. The *p*-nitrophenylhydrazone prepared from this solution yielded, after recrystallisation from 50% alcohol, yellow needles melting at 123–124°, which appeared to consist mainly of the *p*-nitrophenylhydrazone of acetaldehyde, since the melting point was not lowered on admixture with a pure specimen (m.p. 128°) of the latter in various proportions (Found: N, 23.17. Calc. for $C_8H_9O_2N_3$: N, 23.46%). A somewhat lower melting point compared with the pure specimen is to be attributed to the contamination with a minor amount of other ingredient, possibly *p*-nitrophenylhydrazone of propyl aldehyde. Hence the dibromo-derivative used for ozonolysis was likely not to be an individual compound in a state of purity; it contained, besides the main constituent which yielded acetaldehyde on ozonolysis, a minor amount of the bromo-derivative which yielded other aldehyde, such as propyl aldehyde, on ozonolysis.

The barium hydroxide solution in the flasks (b) and (c) was found to contain a precipitate of barium carbonate indicating the formation of carbon dioxide by ozonolysis. Calculating from the quantity of barium carbonate, the yield of carbon dioxide was found to be 6.6% of the dibromo-derivative used for ozonolysis. Assuming that the dibromo-derivative has one of the group $=CH\cdot CH_2\cdot CH=$, and carbon dioxide is formed to a quantitative extent by the secondary decomposition of the products of ozonolysis derived from that group, the yield of carbon dioxide is calculated to be 8.98% of the dibromo-derivative.

(ii) *Decomposition products obtained from aqueous solution* (B). These were a reddish orange liquid. Oxidation with alkaline permanganate followed by acidification yielded succinic acid which showed, on recrystallisation from ethyl acetate, neutr. value 949.1 and m.p. 182–183°.

(iii) *Oily substances* (C). Yield about 6 g. In order to eliminate the bromine from oily substances, these were dissolved in 10 c.c. of methanol and 6 g. of zinc powder was added in several portions. The mixture was refluxed on the water-bath, 10 c.c. of 5 N solution of hydrogen chloride in methanol was gradually added, and the debrominated product was taken up with ether. On removal of the solvent from the ethereal solution, the residue was heated in an oil-bath and there was obtained 1.4 g. of colourless liquid boiling below 180°. This was saponified, the unsaponifiable matter removed by extraction with ether and the free acid liberated. It had neutr. value 435.7 and iodine value 182.7 (calc. for $C_7H_{12}O_2$: neutr. value 438.0, iodine value 198.2), and was considered to consist mainly of heptenoic acid. The hydrogenation product was shown to be heptoic acid by preparing its barium salt (Found: Ba, 34.69. Calc. for $(C_7H_{13}O_2)_2Ba$: Ba, 34.73%).

3. **Ozonolysis of Tetrabromo-derivative of Clupanodonic Acid.** Fifteen g. of clupanodonic acid was dissolved in 150 c.c. of ether, and on cooling, the bromine solution prepared by dissolving 15 g. (calc. for the formation of tetrabromide:

Table 4.

Precipitate	Yield (g.)	Iodine value
1st ppt.	4	68.1
2nd ppt.	11	117.2
3rd ppt.	9.5	119.5
4th ppt.	0.5	119.1
Bromide remaining in the final filtrate	2.5	142.5

14.52 g.) of bromine in 30 c.c. of glacial acetic acid was added with constant stirring. No precipitate was formed after standing for 2 hours. The ethereal solution was washed with water, dehydrated, and on removal of ether there remained 29.5 g. of bromides. These were dissolved in 10 volumes of alcohol, a minute amount of insoluble bromides was removed by filtration, and the filtrate was admixed with water so as to effect a fractional precipitation of the bromides. The yield and the iodine value of each precipitate are shown in Table 4.

The 2nd and 3rd precipitates were combined, and subjected again to the fractional precipitation from alcoholic solution by adding water, by which a tetrabromo-derivative having iodine value 118.0 (calc. for $C_{22}H_{34}O_2Br_4$: 117.2) was separated. Sixteen g. of this bromide was subjected to ozonolysis in the same manner as described above in the case of amyl clupanodonate and dibromo-derivative. The volatile decomposition products (**A**) were made to be absorbed by water in the flask (**a**) and then by barium hydroxide solution in two flasks (**b** and **c**). The decomposition products, which did not volatilise, were separated into two portions: the decomposition products obtained from aqueous solution (**B**) and the oily substances (**C**).

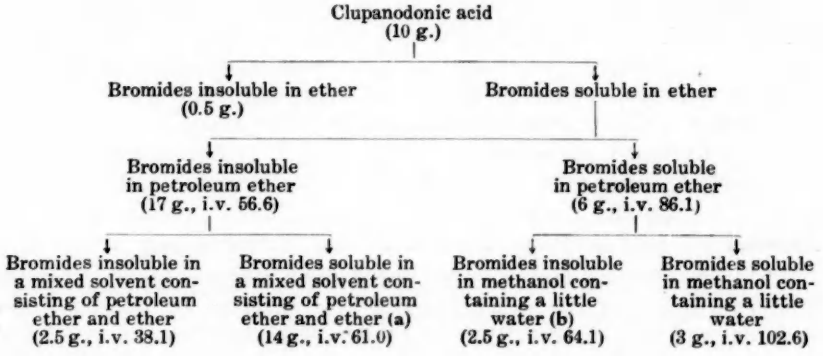
(i) *Volatile decomposition products* (**A**). The aqueous solution in the flask (**a**) showed an aldehyde reaction, and gave a small amount of precipitate on adding *p*-nitrophenylhydrazine. The barium hydroxide solution in the flask (**b**) was found to contain a small amount of the precipitates of barium carbonate, from which the yield of carbon dioxide formed by the ozonolysis was calculated to be 0.69% of the bromo-derivative used for ozonolysis. It is thus seen that volatile aldehyde and carbon dioxide were formed by the ozonolysis, but the yields of these compounds were so small that they were considered to be derived from a minor ingredient contaminating the tetrabromo-derivative, and not from the main constituent.

(ii) *Decomposition products obtained from aqueous solution* (**B**). These were a reddish orange liquid. Oxidation with alkaline permanganate followed by acidification yielded a crystalline product which, after being washed with a little ether, showed m.p. 177–178°, and recrystallisation of this product from ethyl acetate gave succinic acid having neutr. value 945.1 and m.p. 182–183°.

(iii) *Oily substances* (**C**). Yield 11.5 g. These were debrominated with zinc powder and hydrogen chloride in methanol. The debrominated product was distilled, and a fraction boiling in the neighbourhood of 130°/20 mm. was collected separately. This fraction was hydrogenated, saponified, freed from the neutral matter, and the acidic matter was separated which, recrystallised from dilute alcohol, showed neutr. value 324.1 (calc. for $C_{10}H_{20}O_2$: 325.9) and m.p. 29.5–30°. The melting point was not lowered when the substance was admixed with a pure specimen of capric acid, m.p. 30.5–31°, in various proportions.

4. **Ozonolysis of Hexabromo-derivative of Clupanodonic Acid.** Ten g. of clupanodonic acid was dissolved in 100 c.c. of ether, and on cooling, the bromine solution prepared by dissolving 15 g. (calc. for the formation of hexabromide: 14.52 g.) of bromine in 30 c.c. of glacial acetic acid was added gradually with constant stirring. After standing for 2 hours the precipitate of insoluble bromides formed in a minute amount was removed by filtration, and the soluble bromides in an ethereal solution was obtained on distilling off ether. These were subjected to a further separation by means of the solvents as shown in Table 5.

Table 5.



The bromides (a) and (b) were united and treated again with a mixed solvent consisting of petroleum ether and ether, the insoluble portion was removed, the soluble portion was further treated with methanol containing a little water, the soluble portion was discarded; the insoluble portion thus obtained had iodine value 62.0 (calc. for $C_{22}H_{34}O_2Br_6$: 62.7) and it was considered to consist of a hexabromo-derivative.

The hexabromo-derivative (11.5 g.) thus obtained was ozonised in chloroform solution and the ozonide was decomposed with water. Volatile decomposition products were not formed, and the decomposition products were separated into two portions as before, i.e., the products obtained from the aqueous solution and the oily substances. The former consisted of a reddish orange liquid which deposited a crystalline solid at room temperature. Oxidation with alkaline permanganate followed by acidification gave a product which, after being washed with a little cold ether, melted at 178–179° and yielded succinic acid on recrystallisation from ethyl acetate; neutr. value 948.2, m.p. 182–183°. The oily substances (9.5 g.) were debrominated with zinc powder and hydrogen chloride in methanol. Distillation of the debrominated product (2.7 g.) gave 1.3 g. of a distillate boiling below 170°/15 mm. This was hydrogenated and saponified, and the product was separated into acidic and neutral portions in the usual way. The acidic portion, after being recrystallised from 85% alcohol, was shown to be myristic acid $C_{14}H_{28}O_2$; neutr. value 243.7 (calc. 245.8), m.p. and mixed m.p. 53.5–54°. The neutral portion, after being treated with sodium bisulphite solution, showed acetyl value 216.9 (calc. for tetradecanol $C_{14}H_{30}O$: 219.0)

which indicated that it consisted chiefly of higher alcohol. The free alcohol liberated from the acetylated product melted at 30.5–31° after recrystallisation from 85% alcohol. This is considered to consist chiefly of tetradecanol formed by the hydrogenation of the corresponding aldehyde which is likely to be present in the debrominated product, but its melting point is considerably lower than that of pure tetradecanol. Krafft[7] gives m.p. 38° for the same compound.

Summary.

1. Amyl clupanodonate was subjected to ozonolysis. Among the products of ozonolysis were found propyl aldehyde, acetaldehyde, carbon dioxide, succinic acid, amyl hydrogen succinate and also lower acids which were deemed to consist of propionic and acetic acids. Of these compounds, acetaldehyde, acetic acid and carbon dioxide are attributable to the secondary decomposition of the products of ozonolysis primarily derived from the group $=CH\cdot CH_2\cdot CH=$. Accordingly clupanodonic acid was shown to contain the following groups: $CH_3\cdot CH_2\cdot CH=$, $=CH\cdot(CH_2)_2\cdot COOH$, $=CH\cdot CH_2\cdot CH=$ and $=CH\cdot(CH_2)_2\cdot CH=$, of which clupanodonic acid contains three of the last named group.

2. The dibromo-derivative of clupanodonic acid was separated as the chief constituent of the product which was obtained by adding 1 mol bromine to 1 mol clupanodonic acid. Similarly tetrabromo- and hexabromo-derivatives of clupanodonic acid were separated, respectively, as the chief constituents of the product obtained by adding 2 mols and 3 mols bromine, respectively, to 1 mol clupanodonic acid. It is seen from the following results obtained by the ozonolysis of these bromo-derivatives that, in these partial brominations, bromine adds selectively first to the ethylenic linking which is more distant from the carboxyl group. Though this selectivity is not a complete one, any of the above-mentioned bromo-derivatives contains as its chief constituent the product formed in accordance to this selectivity.

3. Ozonolysis of dibromo-derivative of clupanodonic acid thus obtained gave a bromo-compound which on debromination and subsequent hydrogenation yielded, as an acidic product, heptoic acid. This fact, coupled with the results obtained by the ozonolysis of amyl clupanodonate, indicated that clupanodonic acid had the group $CH_3\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=$.

4. Ozonolysis of tetrabromo-derivative of clupanodonic acid gave a bromo-compound which on debromination and subsequent hydrogena-

(7) *Ber.*, (1883), 1714.

tion yielded capric acid, and consequently clupanodonic acid was shown to contain the group $CH_3{\cdot}CH_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH{=}$.

5. Ozonolysis of hexabromo-derivative of clupanodonic acid gave a bromo-compound which on debromination and subsequent hydrogenation yielded myristic acid, and consequently clupanodonic acid was shown to contain the group $CH_3{\cdot}CH_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}$.

6. From the foregoing results, the constitution of clupanodonic acid has been established as $\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16,\ 19:20}$-docosapentenoic acid which is expressed by the following formula:

$$CH_3{\cdot}CH_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}COOH.$$

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

SURFACE POTENTIAL DIFFERENCES OF UNIMOLECULAR FILMS OF FATTY ACIDS.

By **Yohei YAMAGUCHI** and **Saburo MIZUNO.**

Received June 3rd, 1935. Published September 28th, 1935.

Introduction.

The measurement of the surface potential difference between air and aqueous solutions of many electrolytes was first studied by Bichat and Blondlot[1] in 1883. Later Kenrick[2] measured the electromotive force of the following type of cells coupled with various inorganic salt solutions:

n. KCl | solution A | air gap | solution B | n. KCl

where the solution A of a certain electrolyte was dropped from a jet placed at the upper part of the axis of the vertically suspended cylinder and insulated from the solution B by an air gap. The solution B of another electrolyte, or of the same electrolyte as A but of different con-

(1) Bichat and Blondlot, *J. physiq.*, [2], **11** (1883), 548.
(2) Kenrick, *Z. physik. Chem.*, **19** (1896), 625.

centration, was flowed very slowly to cover the inner wall of the vertical cylinder. There was found a parallelism between the variation of the surface potential difference with the concentration of the solution of electrolyte and its surface activity.

Since Guyot[3] and Frumkin[4] succeeded independently in measuring the surface potential more accurately and quantitatively, devising an ingenious apparatus, many researches were carried out in this field by several investigators, such as Rideal,[5] Adam,[6] Fosbinde,[7] Zisman,[8] Harkins,[9] and their collaborators. In all these experiments of the above authors a platinum electrode coated with polonium or ionium was used as an ionizer of the air gap instead of Kenrick's dropping electrode, and from the measured surface potentials of the liquids the state of films of polar substances was discussed.

In the present experiment X-ray was used to ionize the air gap instead of radioactive elements. This method was already adopted in 1931 by Yoshikazu Tsunoda and one of the present authors for the study of the similar subject at the same laboratory. X-ray was emitted from an ordinary Coolidge tube and allowed to pass through the air space between the surface of the solution on which a film of fatty acid was spreaded and the platinum disk placed in the air parallel to this surface. Thus the potential differences between air and the films of stearic, oleic, and trichloroacetic acids on 0.02 N KCl aqueous solution were measured respectively. The results, however, were not published.

In the next year 1932 Hayato Shigeno[10] studied the unimolecular films of several fatty acids by the same method, simplifying the apparatus by using a glass dish instead of the funnel used by Tsunoda and others. The present study is to complete this X-ray ionization method by using the former apparatus with a few improved points.

---

(3) Guyot, *Ann. physiq.*, [10], **2** (1924), 506.

(4) Frumkin, *Z. physik. Chem.*, **109** (1924), 34; *ibid.*, **116** (1925), 485; *ibid.*, **123** (1926), 321. Frumkin and Williams, *Proc. Nat. Acad. Sci.*, **5** (1929), 400.

(5) Schulmann and Rideal, *Proc. Roy. Soc.*, A, **130** (1930), 259, 270, 284. Lyons and Rideal, *ibid.*, **124** (1929), 323. Schulmann and Hughes, *ibid.*, **138** (1932), 430. Whally and Rideal, *ibid.*, **140** (1933), 484, 489, 497.

(6) Adam and Harkins, *ibid.*, **138** (1932), 411; *Trans. Faraday Soc.*, **29** (1933), 90, 837. Adam and Miller, *Proc. Roy. Soc.*, A, **142** (1933), 401.

(7) Fosbinder and Lessing, *J. Franklin Inst.*, **215** (1933), 425.

(8) Zisman and Yamins, *J. Chem. Phys.*, **1** (1933), 656.

(9) Harkins and Fischer, *J. Chem. Phys.*, **1** (1933), 852.

(10) H. Shigeno, the results were not published.

Experimental.

The measurement of the surface potential is based upon the principle of ionizing the air space between the platinum electrode and the fatty acid film on the KCl solution by X-ray, and the potential difference between the elctrode and the film is obtained by the compensation method by using Lindemann electrometer which is suitable for this experiment owing to its small capacity. The apparatus and the operation are as follows.

At first a certain quantity of the substrate solution is poured into the glass dish (A) and mounted on the ebonite platform (E); it is raised to a certain height by the screw (S), so that the junction tip (T) of the

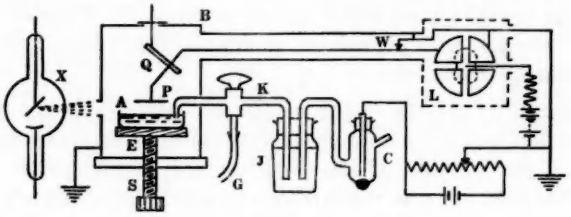


Fig. 1.

connecting tube reaches the surface of the substrate solution and the width of the air gap between the platinum electrode and the solution is reduced to a few millimeters. The substrate solution in the dish (A) is connected to the calomel half cell (C) through the three way cock (K) and the reservoir (J) which contains 0.1 N KCl solution. The liquid junction is made in the three way cock by drawing the solution with the rubber tube (G). After the lid of the brass cover was shut, X-ray of a certain intensity is emitted through the slit into the air gap between the electrode and the solution, and the contact point (W) previously grounded is disconnected. Adjusting the potentiometer so that the needle of the Lindemann electrometer indicates its original position (zero point) which was found at the grounded needle, the potentiometer is read. The current of the Coolidge tube and the primary voltage of the high tension transformer are also observed. Thus the measurement of the surface potential (v) of the pure substrate solution is carried out.

The vessel (A) is now carefully taken outside the brass cover and a few drops of the very dilute solution of the fatty acid in petroleum ether is dropped from the small capillary pipette previously calibrated. The petroleum ether is allowed to evaporate and the thin film of the fatty acid is made on the solution. The dish is again screwed up to the

former position and the surface potential is measured as before. The difference of this value and the former gives the surface potential of the fatty acid film at the concentration known from the number of drops added.

Preliminary Experiment. (1) *The cleanness of the vessel* (A). The cleanness of the vessel is one of the most important factors to obtain reproducible results. Before every measurement all vessels are washed several times with sulphuric acid chromate mixture and then with ordinary water and finally rinsed with distilled water. In washing, good care must be taken not to touch the vessels with fingers by using two glass rods, otherwise fat on the skin spreads rapidly on the wet surface of the vessel and causes a great error in the measurement. The vessels thus washed are placed on sheets of filter paper and dried at room temperature overnight.

(2) *The effect of the width of the air gap.* The variation of the surface potential with the change of the distance between the platinum electrode and the surface of the solution was investigated. The most favourable distance for the measurement is 6–7 mm., and an increase of 10 mm. in distance gives 30–40 mv. increase in potential, i.e. the reading of the potentiometer increases as if a large resistance were put in the air gap.

(3) *The upper limit of the range of the X-ray radiation in the air gap.* The influence of the height of the X-ray radiation on the surface potential of the fatty acid film was investigated. It was found that when the upper range of the radiation is kept at a level the same as, or slightly higher than, that of the platinum electrode, the measured potenial difference is not altered, but when the holder of the electrode is illuminated the measured potential decreases about 10 mv. or more owing to the leakage between the electrode and the grounded brass box. Hence all experiments are carried out at the best condition of the X-ray radiation, i.e. the upper range being kept at the same height as the platinum electrode.

(4) *The decrease of the surface potential with time.* Although the vessel is sufficiently washed, the surface potential decreases gradually with time. But when the junction tip (T) is drawn out from the solution and again dipped into another position of the surface, the potential difference which was once decreased regains the value near the original one. This phenomenon is reproducible during at least half an hour.

(5) *The influence of the hardness and the intensity of X-ray.* The intensity of X-ray is represented by the current of the Coolidge tube and its hardness is proportional to the voltage of the high tension side of the transformer. The effects of these factors on the surface potentials were examined by altering the current and the tension of the X-ray producing apparatus. It was found that there are no perceptible changes or deviations of the surface potential of fatty acid film, when the current of the Coolidge tube is 0.6–1.6 milliamp. and the primary voltage of the X-ray transformer is 70–85 v. Therefore all experiments were carried out at the following conditions: the current of the Coolidge tube about 1.0 milliamp. and the primary voltage of the X-ray transformer about 70 volts.

(6) *The sensibility of the Lindemann quadrant electometer.* The sensibility of the Lindemann electrometer used was already studied by Tsunoda and examined again before the experiment. It depends principally on the applied needle potential and the humidity of the atmosphere. The following results were obtained at the sufficiently good dryness.

Needle potential (v.)	43.5	42.0	40.5	38.6	36.7	34.8	33	31	30
Division/100 mv.	7.7	5.1	3.8	2.7	2.1	1.9	1.3	1.1	0.9

(7) *The concentration of fatty acids.* Fatty acids used for the experiment are myristic, palmitic, stearic, and oleic acids, having melting points 53.8, 60.8, 69, and 14°C. respectively. These acids are weighed and dissolved into purified petroleum ether and diluted further with 20 or 30 times of the same solvent in such dilution that the acid in one drop of the solution from the capillary pipette gives the surface concentration of about 1×10^{-10} g. mol/cm.^{2} after the evaporation of the solvent on the surface of the substrate solution. The volume of one drop from the pipette is about 0.01 c.c. The petroleum ether employed was a product from N. P. C. It was distilled three times and the fraction between 35 and 50°C. was collected.

Measurements and Experimental Results. All experiments were carried out under the following conditions: temperature 17–20°C., substrate solution 0.01 N KCl or 0.11 N HCl, current of Coolidge tube 1.0 milliamp., primary voltage of transformer 70 volts, and needle potential 42 or 43 volts.

The surface potential of the substrate solution is measured at first under the above conditions and by the experimental manipulations already described. A certain number of drops of petroleum ether solution of the fatty acid is then added on the substrate solution and the film of the fatty acid with a certain surface concentration is formed on the solution

Table 1.

Myristic acid			Palmitic acid		
Surface conc. ($n\times10^{-10}$ g. mol/cm^2.)	Substrate solution		Surface conc ($n\times10^{-10}$ g. mol/cm^2.)	Substrate solution	
	0.111 N HCl 17°C.	0.01 N KCl 18°C.		0.111 N HCl 18°C.	0.01 N KCl 17°C.
	Pot. dif. ΔV (mv.)	Pot. dif. ΔV (mv.)		Pot. dif. ΔV (mv.)	Pot. dif. ΔV (mv.)
0.93	66.6 35.5	—	1.76	191 176 164	119 111
1.87	103 75.5	—	2.64	210 221 234	166 124 123
2.80	98 136	42.5 50.5	3.52	230 242 248	188 190 172
3.74	138 138	49 64.7	4.40	276 270	222 200
4.67	205 194	106 105	5.28	304 304 283	245 218
5.60	243 228	160 164	6.16	305 338 335	245 255 256
6.54	313 270	177 204	7.04	337 337 338	251 261 257
7.47	325 302	236 268	7.92	348 350	262 256
8.41	323 345	268 275	8.80	358	263
9.43	360 360	268	10.56	335	265
12.14	353	271	11.44	—	262
14.01	360	270	13.2	—	257

Table 1 (*Concluded*).

Stearic acid			Oleic acid		
Surface conc. ($n\times10^{-10}$ g. mol/cm².)	Substrate solution		Surface conc. ($n\times10^{-10}$ g. mol/cm².)	Substrate solution	
	0.111 N HCl 18°C.	0.01 N KCl 18°C.		0.111 N HCl 17°C.	0.01 N KCl 17°C.
	Pot. dif. ΔV (mv.)	Pot. dif. ΔV (mv.)		Pot. dif. ΔV (mv.)	Pot. dif. ΔV (mv.)
0.95	45 74	74 81	1.03	107 111	38 53
1.90	120 126	153 145 145	2.06	129 124 128	82 81
2.85	167	200 208 204	3.09	151 147 168	95 106 101
3.80	258 249	243 245 242	4.12	190 198 177	137 146 144
4.75	300 318	248 262.	5.15	223 239 204	160 177 186
5.70	320 316	280 289 300	6.18	228 230 230	162 194 153
6.65	348 350	304 300	7.21	253 240	173 189 169
7.60	354 348	314 302	8.24	250 248	188 193
8.55	—	300	9.27	—	190
9.50	355	312 306	10.3	257 256 253	176 185
11.40	358	—	15.45	262 265 262	203 184

by allowing the petroleum ether to evaporate. Finally the surface potential of the film is measured under the same experimental conditions as in the former measurement.

The variation of more than 10 mv. is hardly found in the measured values of the substrate solution without the film. Variations of about

40 mv. are, however, often found in the case of the solution with fatty acid film on it. This large variation is generally found in the case of the small surface concentration giving non-uniform film on the whole surface. In the case of larger concentration probably giving an uniform film on the surface, there is scarcely found a variation over 10 mv. The difference between the mean value of the measured values of the solution with the film and that of the solution without the film is taken as the surface potential difference of the fatty acid film of the surface concentration evaluated from the number of drops added.

Such surface potential differences as the above-mentioned have been obtained from the experimental data for the four fatty acids and these values are shown in Table 1. The first column of the table indicates the surface concentrations of the fatty acid, and the second the surface potential differences in mv. The relations between the potential differences and the surface concentrations are shown graphically in Fig. 2–5. The abscissa of the graphs indicates the surface concentrations (n) in 10^{-10} g. mol/sq. cm., and the ordinate the potential differences (ΔV) in mv. The curve A is the relation obtained by using 0.11 N HCl as the substrate solution and the curve B is that by 0.01 N KCl.

(1) *Myristic acid.* Fig. 2 shows the relation between the surface potential difference of myristic acid film on the solution and its surface concentration. The curve drawn with the dotted line in the figure was plotted with the data obtained by Harkins[11] for the same acid film. Although these data were obtained by Harkins by using 0.01 N HCl as the substrate solution and by an entirely different method, the resulting curve C shows good agreement with curve A. It is found that the two curves A and B are parallel with each other and have almost uniform inclinations.

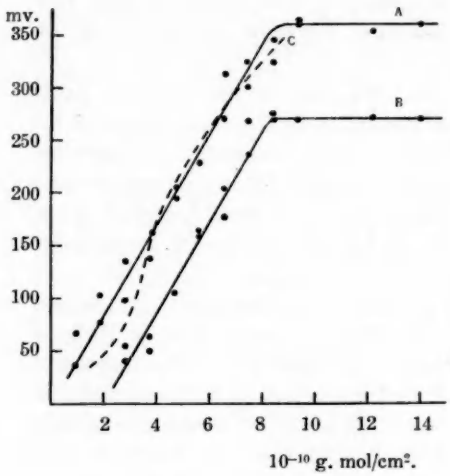
The following well-known formula of Helmholtz is now applied to this case:

$$\Delta V_1 - \Delta V_2 = 4\pi(n_1 - n_2)\bar{\mu} ,$$

where ΔV represents the surface potential difference, n the number of molecules on 1 sq. cm., and $\bar{\mu}$ the mean vertical component of dipole moment. From this formula it may be seen that $\bar{\mu}$ indicates the slope of the ΔV–n-curve, namely the inclination of the (surface potential)—(surface concentration)-curve.

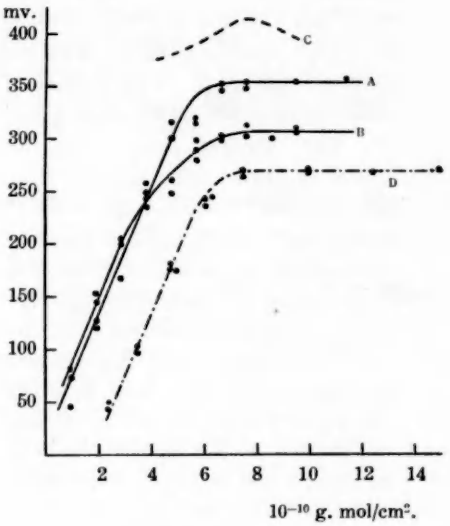
From the fact that two curves A and B are parallel and have the same inclination, it may be considered that the mean vertical component

(11) Harkins, *J. Chem. Phys.*, **1** (1933), 858.



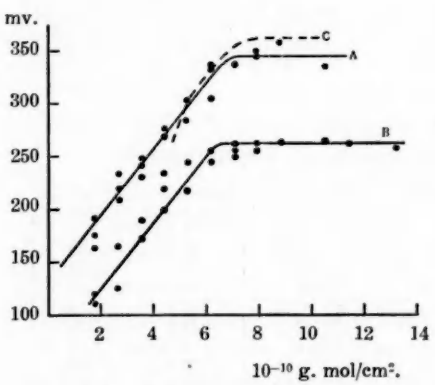
Myristic Acid

Fig. 2.



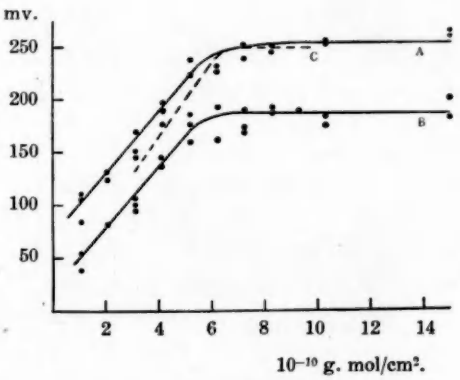
Stearic Acid

Fig. 4.



Palmitic Acid

Fig. 3.



Oleic Acid

Fig. 5.

of dipole moment $\bar{\mu}$ of myristic acid has the same value and alter neither with the surface concentration nor with the substrate solution.

(2) *Palmitic acid.* The results obtained with palmitic acid are plotted in Fig. 3. There is also parallelism between curves A and B and the coincidence of A and C.

(3) *Stearic acid.* Fig. 4 shows the curves for stearic acid. Curve D drawn with a chain line was plotted with the data obtained by Y. Tsunoda[10] with 0.02 N KCl as the substrate solution. Comparing these four curves, if the values of curves A and D are correct, those of B and C are a little higher and if B and C are correct, A and D are a little lower. The slopes of curves A, B, and D, however, are almost similar to one another.

(4) *Oleic acid.* Fig. 5 shows the curves for oleic acid. If a curve be drawn with the data obtained by Y. Tsunoda with 0.02 N KCl as the substrate solution, it falls nearly on curve B, although the former is not drawn in the figure. It is found that curves A and B are parallel as before and curve C falls nearly on A. It is very remarkable in this case that the maximum surface potential attainable is about 100 mv. less than those of the former three fatty acids.

Assuming the surface potentials of the fatty acid films of the same surface concentration are nearly proportional to their length of the molecules or their dipole moments, and basing on the fact that the saturated surface potential of oleic acid film is about 100 mv. less than that of stearic acid with the same number of carbon atoms (18) in the molecule, it may be considered that the vertical length of the former on water is smaller than that of the latter by the amount corresponding

Table 2.

Fatty acid	M.p.	Mean vert. comp. dipole moment ($\bar{\mu}\times10^{-19}$ e.s.u.)	Saturation point		
			Subs. sol.	Area (sq. Å per mol.)	Pot. dif. (mv.)
Myristic acid $CH_3(CH_2)_{12}COOH$	53.8	1.89	HCl KCl	19.6 20.0	360 270
Palmitic acid $CH_3(CH_2)_{14}COOH$	60.8	1.37	HCl KCl	26.4 28.3	340 260
Stearic acid $CH_3(CH_2)_{16}COOH$	69	2.68	HCl KCl	27.0 27.0	350 310
Oleic acid $CH_3(CH_2)_7CH{=}CH{\cdot}(CH_2)_7COOH$	14	1.27	HCl KCl	27.0 30.0	250 190

to this value. This can be explained from the fact that oleic acid has a double linkage in the central part of the molecule and is folded at this point. The mean vertical component of dipole moment ($\bar{\mu}$) is calculated from Helmholtz's formula for the four fatty acids and shown in Table 2. The value for stearic acid is about 2.7×10^{-19} e.s.u., while that of oleic acid is ca. 1.3×10^{-19} e.s.u. and about half that of stearic acid.

Discussion.

The characteristic values calculated from the measured results of the four fatty acids are summarized in Table 2. The third column of the table is the mean vertical component of dipole moment ($\bar{\mu}$) calculated from Helmholtz's formula. The fifth and sixth columns are the area per molecule in sq. Å and the surface potential at the saturation point respectively. It is found that there is always a saturation curve in the (surface potential)—(surface concentration)-curve of the fatty acids. The break point on the curve, i.e. the starting point of the saturation is nearly similar for all the acids and is about 27 sq. Å per molecule and this is the value of the order of a molecular dimension. From this fact it may be considered that at this break point the unimolecular film of fatty acids is established, and in the range of larger area per molecule than that of the break point, i.e. in the inclined part of the curve, the film is in the expanded state and the potential difference changes nearly proportional to the surface concentration. And in the range of smaller area per molecule than the break point, i.e. in the horizontal part of the curve, the film is in the condensed or liquid state as former investigators already described. At extreme concentration, the film is transformed into solid state and sometimes it is considered that small crystals of fatty acid are locally floating on the film.

The maximum or saturation potentials of the saturated fatty acids are almost nearly equal, about 350 mv., but in fact there should be a certain difference in potentials, i.e. about 20–30 mv. for one carbon atom in fatty acid as stated by Harkins and others. Comparing the mean vertical component of dipole moment of fatty acids, that of stearic acid with the largest number of carbon atoms is greatest in value and that of oleic acid is nearly half that of stearic acid, since the length of the molecule of the former is shortened owing to the fold at the point of the double linkage at the central part of the molecule in spite of the same number of carbon atoms.

The value of palmitic acid is less than that of stearic acid. However the value for myristic acid and that for palmitic acid are reversed if the numbers of carbon atoms in them are compared.

One of the authors studied on the similar subject by using a different method of ionizing the air gap at the Physico-chemical Laboratory of University College, London, with the encouragement of Prof. F. G. Donnan to whom he wishes to express his cordial thanks.

Summary.

(1) Gas—liquid interfacial potential difference of fatty acid film was measured by using the method of ionizing air gap between the electrode and the surface of the liquid with X-ray.

(2) Various factors which affect the measurements were studied at first.

(3) Under the most favourable conditions the measurements of the surface potentials were carried out with four fatty acids, i.e. myristic, palmitic, stearic, and oleic acids.

(4) The surface potential difference attains a maximum or a saturation value at a certain definite surface concentration. This value is nearly equal for three saturated fatty acids and is about 350 mv. The value for oleic acid, however, is about 240 mv.

(5) The (surface potential)—(surface concentration)-curves were plotted and the mean vertical component of dipole moment was calculated for these fatty acids by applying Helmholtz's formula.

(6) The break point of the curve or the saturation point of fatty acid is nearly similar for four acids, and the area occupied by a molecule at this point is about 27 sq. Å.

Chemical Institute, Faculty of Science,
Tokyo Imperial University, Tokyo.

DIE KONZENTRATION DER SCHWEREN ISOTOPE IN ZELLULOSEN.

Von Kenzo OKABE und Toshizo TITANI.

Eingegangen am 26. August, 1935. Ausgegeben am 28. September, 1935.

Aus dem Versuch mit einigen Kohlenhydrat-haltigen Substanzen kamen Titani und Harada[1] zur Vermutung, dass schwere Isotope, höchstwahrscheinlich Deuterium, allgemein in allen Kohlenhydraten konzentriert vorhanden sind. Um diese Ansicht weiter zu prüfen, untersuchten wir jetzt einige Zellulose-haltige Substanzen auf ihren Gehalt an schweren Isotopen. Die untersuchten Substanzen waren Filtrierpapier, Baumwolle, Zedernholz und Bambus. Jede Substanz wurde zunächst bei 100°C. in Luft gut getrocknet. Sie wurde dann im Luftstrom verbrannt, und das erhaltene, abdestillierte Wasser wurde sorgfältig nach der früher beschriebenen Weise[2] gereinigt. Das spezifische Gewicht des so gereinigten Wassers verglichen wir mit nach gleicher Weise gereinigtem Osaka-Leitungswasser bei 8.5°C. durch die Schwebemethode mittels eines Quarzschwimmers. Die nebenstehende Tabelle 1 zeigt die gefundenen Differenzen in γ Einheiten ($\gamma = 10^{-6}$) im Vergleich mit dem Standardwasser.

Die Messung für Filtrierpapier wurde von Dr. Harada durchgeführt. Jedes Resultat ist der Durchschnitt aus zwei bis drei Messungen. Aus der Tabelle ersieht man schon, dass schwere Isotope, vermutlich Deuterium, auch in diesen Substanzen in gleicher Menge wie bei den früher untersuchten Kohlenhydrat-haltigen Substanzen konzentriert vorhanden sind. Die Zunahme des spezifischen Gewichts über das des Standardwassers ist umso grösser je reicher die Substanz an Zellulose ist.

Tabelle 1.

Substanz	Differenz
Filtrierpapier	+6.3 γ
Baumwolle	+5.7 γ
Zedernholz	+4.5 γ
Bambus	+4.4 γ

Es wurde von einigen Autoren[3] darauf hingedeutet, dass das Deuterium in den wachsenden Teilen der Pflanzen, z. B. in jungem

(1) T. Titani und M. Harada, dies Bulletin, **10** (1935), 205, 261.

(2) *Ebenda.*

(3) E. W. Washburn und E. R. Smith, *Bur. Standards J. Research*, **12** (1934), 305; *Science*, **79** (1934), 188, 454; H. J. Emeléus, F. W. James, A. King, T. G. Pearson, R. H. Purcell und H. V. A. Briscoe, *J. Chem. Soc.*, **1934**, 1207.

Weidenholz angereichert ist. Als ein solches Beispiel prüften wir Bambussprösslinge. Weil sie sehr schnell wachsen, kann man eine merkliche Anreicherung des Deuteriums in denselben erwarten. Einige Sprösslinge wurden direkt aus dem Feld gezogen, und Schale, Inhalt sowie Presssaft aus dem letzteren wurden gesondert untersucht. Die beiden erst genannten Teile wurden im Luftstrom verbrannt und das abdestillierte Wasser wurde zur Prüfung benutzt. Die Messresultate gibt Tabelle 2 wieder. Dabei muss man die folgenden Tatsachen in Rechnung ziehen. Erstens war der Presssaft stark von den Inhaltssubstanzen verunreinigt. Zweitens war der Inhalt sehr saftreich und es blieb sogar nach dem Pressen noch eine reichliche Menge von Saft darin zurück. Zieht man diese Verhältnisse in Rechnung, dann würde sich der Presssaft etwas leichter, dagegen das Wasser aus dem Inhalt noch schwerer erwiesen. Natürlich darf man nicht aus diesem einzigen Beispiel zu weitgehende Schlüsse ziehen. Aber mindestens darf man in diesem Fall wohl vermuten, dass die Anreicherung der schweren Isotope im Bambussprössling nicht mit dem Wachstum sondern vielmehr mit der allgemein vorhandenen Anreicherung der schweren Isotope in Kohlenhydraten in Zusammenhang steht.

Tabelle 2.

Teil der Sprösslinge	Differenz
Schale	+4.4 γ
Inhalt	+0.6 γ
Presssaft	+1.0 γ

Für die finanzielle Unterstützung sind wir der Gakujutsu-Shinkokai (der Notgemeinschaft der Japanischen Wissenschaft), sowie der Hattori-Hohkohkai (der Hattori-Stiftung) zum besten Dank verpflichtet.

Physikalisch-Chemisches Laboratorium
der Kaiserlichen Universität zu Osaka
und
Schiomi Institut für Physikalische
und Chemische Forschungen.